transition metal perchlorates with a substituted porphine base in glacial acetic acid (containing 0.05% water) exhibit an order of decreasing strength as Lewis acids in which Cu > Co > Ni > Mn.[10] This sequence is very similar to the corresponding order of stability of the acetates given above.

The formation constants for the $MOAc^+$ species in aqueous solutions of periodic group IIA elements conform to the same stability sequence as the uncharged acetate in acetic acid,[11] Mg > Ca > Sr > Ba. This is consistent with the conclusion of George and McClure[12] that the relative contribution made by the oxygen atom in the ligand to the stabilization energy is essentially the same in aquo and carboxylate complexes.

Acknowledgment.—We are indebted to the National Science Foundation for financial support of this investigation, under the Research Participation for College Teachers program, NSF GE-350, at Kansas State University.

[10] E. Choi and E. Fleischer, *Inorg. Chem.*, **2**, 94 (1963).

[11] G. Nancollas, *J. Chem. Soc.*, 744 (1956).

[12] P. George and D. McClure, *Progr. Inorg. Chem.*, **1**, 451 (1959).

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Structure Relations in Mixed Metal Oxides

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The layer model for complex metal oxides is used for cases in which oxygen and large cations are essentially close packed and in the ratio of three oxygens to one large cation. The relationships between various layer sequences and the stoichiometry of the compounds, cation interactions, and octahedral site vacancies are discussed. A twelve-layer model for compounds $A_4^{II}Re_2B^{II}O_{12}$ is consistent with the arguments advanced and with the experimental evidence so far obtained.

Introduction

Framework Picture of ABO_3.—In the synthesis of ternary oxides, we have been concerned mainly with compounds containing both large and small cations. The most usual structure among these is the perovskite type with the ideal formula ABO_3 where A is the large cation and B the small cation. The structure may be regarded as derived from the ReO_3 structure in which the B cations are at the corners of the cube; the A cations occupy the body centers. This is a useful way to look at the structure, because in many compounds deficiencies in A cations and to some extent in oxygen may occur, but deficiencies in B cations are not found.

Layer Picture of ABO_3.—For the purpose of this paper, however, it will be more convenient to consider the structure as derived from the close packing of layers of composition AO_3 (Fig. 1). The A cations may be thought of as lying at the corners of the basal plane of a hexagonal cell with oxygens on the edges and in the face center. Close packed stacking of these layers leads to the formation of one octahedron of oxygens for each AO_3 unit. With cubic stacking, these octahedra share corners; with hexagonal stacking, they share faces.

Cubic Closest-Packed Stacking Only

The hexagonal cell for cubic closest-packed stacking is shown in Fig. 2. Two cubic cells are outlined. A cube body diagonal is in the hexagonal *c*-axis direction. The contents of the hexagonal 110 plane are shown in Fig. 3. A diagrammatic representation of this simple perovskite structure is shown in Fig. 4. The packing, cubic with layer sequence *xyz*, is given at the left (*x*, *y*, *z* are used to designate the layers rather than the usual *A*, *B*, *C* to avoid confusion with the cation designations). In the middle of the figure the occupancy of the octrahedral sites with B cations is indicated. The letter "c" is used to designate a "cubic" layer, *i.e.*, a layer for which the two neighboring layers are of different types (*x* and *y*, *y* and *z*, or *x* and *z*). The letter "h" will be used to designate a "hexagonal" layer, a layer for which the two neighboring layers are of the same type (both *x*, both *y*, or both *z*). The sequence of B cations is also shown at the right of the figure as they appear in the 110 plane of the corresponding hexagonal cell. With cubic close packing the B cations lie on a diagonal line corresponding to the cubic axis of the crystal. The hexagonal unit cell consists of three AO_3 layers. Forms of lower symmetry (orthorhombic, rhombohedral, tetragonal. . .) may be regarded as more or less slight modifications of this ideal structure.

Two Different B Cations.—The introduction of two different B cations in the same phase is facilitated by a large difference in charge of the two ions. This may occur at definite compositions in most cases fixed by stoichiometry. The widest variation is possible when the B cations have an average valence of four. Many compounds have been made corresponding to the formulas (a) $A^{II}_2B^{I}B^{VII}O_6$, (b) $A^{II}_2B^{II}B^{VI}O_6$, (c) $A^{II}_2B^{III}B^{V}O_6$, but few have been prepared where both B cations are tetravalent. The structure adopted

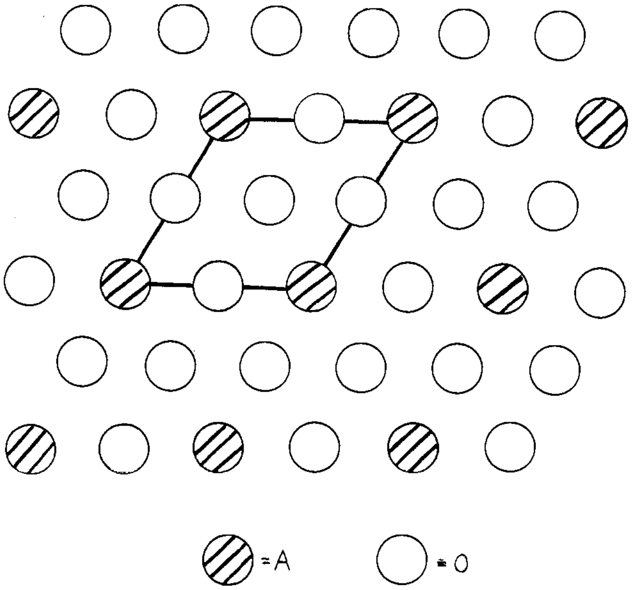

Fig. 1.—AO_3 layer.

by these compounds is the ordered perovskite structure given in Fig. 5. The ordering of the B cations leads to a hexagonal cell of six layers.

The Madelung energies of these phases show a substantial increase with increasing difference in charge of the B cations as shown by the calculations by Rosenstein and Schor[1] given in Table I. This gain in lattice energy is obviously an important factor in the synthesis of these compounds. It is remarkable that the ignition of a mixture of barium carbonate, sodium carbonate, and osmium metal in air leads to complete and rapid conversion to $Ba_2NaOs^{VII}O_6$. Not only is the loss of osmium as the volatile OsO_4 prevented, but also the osmium is stabilized in the unusual heptavalent oxidation state. The lack of any energy advantage in the combination of tetravalent B cations would account for the difficulty of preparation of such phases.

TABLE I
MADELUNG ENERGIES FOR IDEALIZED ORDERED CUBIC PEROVSKITES[1]
$A^{II}{}_2B^{(IV-n)}B^{(IV+n)}O_6$

		Supercell edge,	Madelung energy, kcal./mole	
n	Compound	Å.	Ordering	Total
0	$Ca_2Ti_2O_6$	7.68	. . .	8561
1	$Ba_2Sc^{III}Re^{V}O_6$	8.16	142	8199
2	$Ba_2Ni^{II}Re^{VI}O_6$	8.04	577	8755
3	$Ba_2Li^{I}Re^{VII}O_6$	8.12	1286	9383

A large variety of B cations may be introduced by appropriate pairing. The periodate Ba_2NaIO_6 may be precipitated from solution. $BaMgTeO_6$ is formed as a fine yellow powder at 1200°. Sr_2CrSbO_6 is stable above 1000°. In the first of these compounds to be recognized, Ba_2BaWO_6,[2] one of the B cations is the same as the A cation. The most interesting combinations, however, are those of paramagnetic B cations.

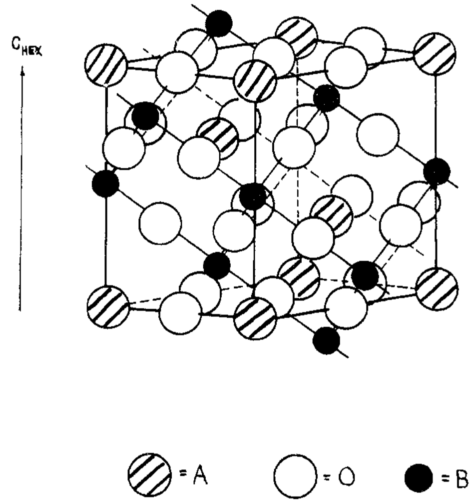

Fig. 2.—Hexagonal cell for cubic closest-packed stacking. Two cubic cells outlined.

Ferrimagnetic interaction has been observed in several instances. A list of these is shown in Table II. It is noteworthy that superexchange interactions involving fifth and sixth period elements can be brought about in these phases. Ordered phases have been observed with other proportions of different B cations. Thus $Ba_3SrTa_2O_9$ was found[3] to have an ordered structure involving three cubic close packed layers as shown in Fig. 6. This kind of order is difficult to achieve, probably because it leads to a rather poor local charge balance. The oxygens in the layer between the tantalum ions carry net charges of $+{}^1/_3$, those between the strontium and tantalum ions $-{}^1/_6$. Recently other phases with this arrangement have been reported.[4]

TABLE II
FERRIMAGNETIC COMPOUNDS WITH THE ORDERED PEROVSKITE STRUCTURE

Compound	Neèl temp., °C.	Saturation moment
Ba_2ReFeO_6	43[a]	1.15[b]
Sr_2ReFeO_6	128[a]	1.26[b]
Ca_2ReFeO_6	265[a]	1.01[b]
$(Ba,K)_2ReMnO_6$	−137[a]	0.58[b]
Sr_2ReMnO_6		0.75[b]
Ca_2ReMnO_6		0.23[b]
Ba_2MoFeO_6	64[c]	
Sr_2MoFeO_6	146[c]	
Ca_2MoFeO_6	104[c]	
Sr_2MoCrO_6	200[c]	
Ca_2MoCrO_6	−125[c]	
Sr_2WCrO_6	180[c]	
Ca_2WCrO_6	−130[c]	

[a] J. Longo and R. Ward, *J. Am. Chem. Soc.*, **83**, 2816 (1961). [b] A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, **1**, 245 (1962). [c] F. K. Patterson, C. W. Moeller, and R. Ward, *ibid.*, **2**, 196 (1963).

With some transition metal ions, it is possible to vary proportions of different B cations if the valences can adjust to compensate for the changes. Thus the proportion of Fe and Re in the phase $Sr_2Fe^{II}Re^{VI}O_6$

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(1) R. D. Rosenstein and R. Schor, *J. Chem. Phys.*, **38**, 1789 (1963).

(2) E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **4**, 503 (1951).

(3) F. Galasso, J. R. Barrante, and L. Katz, *J. Am. Chem. Soc.*, **83**, 2830 (1961).

(4) F. Galasso and J. Pyle, *Inorg. Chem.*, **2**, 482 (1963).

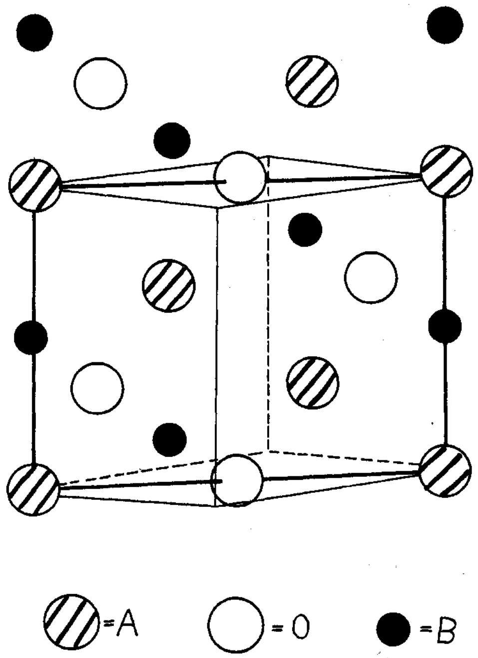


Fig. 3.—Atoms of hexagonal 110 plane for cubic closest-packed stacking. The hexagonal cell is outlined.

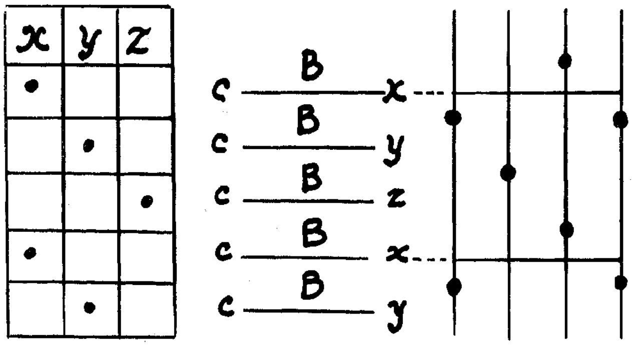


Fig. 4.—The simple perovskite ABO_3.

may be changed to $Sr_3Fe^{III}_2Re^{VI}O_9$ without changing the basic structure. The intensity of the superlattice lines, however, decreases progressively with increase in the proportion of iron.

Most of the ternary oxides of the ordered perovskite types have been prepared with an alkaline earth cation as the A cation. It would seem reasonable to suppose that compounds of the type $A^{I}_2B^{III}B^{VII}O_6$, $A^{I}_2B^{IV}B^{VI}O_6$, $A^{III}_2B^{I}B^{V}O_6$, and $A^{III}_2B^{II}B^{IV}O_6$ could also be made. The greater charge difference would again be a major factor in obtaining the compounds. Perhaps a ferrimagnetic compound of osmium(VII) such as K_2CrOsO_6 could be prepared in this way. The choice of ions, however, is going to be much more restricted than in the $A^{II}B^{IV}O_3$ compounds.

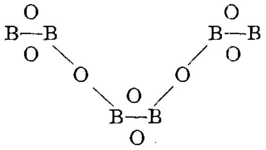
Hexagonal Closest-Packed Stacking Only

Hexagonal close packing of the AO_3 layers is found in the compound $BaNiO_3$,[5] the structure of which is shown in Fig. 7. The nickel ions are in close proximity to each other (2.42 Å.), which suggests the possibility of metal–metal bonding. The structure is not a common one among the oxides. The only other oxides reported to have this structure are $BaCoO_{3-x}$[6] and the low temperature form of $BaMnO_3$.[6,7] Recently $BaTiS_3$ has been shown to have this structure.[8]

Mixed Cubic Hexagonal Closest-Packed Stacking

When we come to consider sequences of layers having both cubic and hexagonal close packing, there would seem to be an almost unlimited number of possible combinations. If we assume, however, that the change from cubic to hexagonal close packing occurs as a result of metal–metal interaction, the number of likely combinations might be quite limited.

Periodic Switching of Stacking Schemes.—Face sharing of octahedra may result from an attractive metal–metal interaction strong enough to overcome the repulsive metal–metal charge interaction. Extended strings of face-sharing octahedra are uncommon, however. Alternation in corner sharing and face sharing of octahedra might involve some kind of asymmetry in the bond orbitals of the interacting B cations. Such an alternating sequence could be represented schematically as shown below



where O above and below a bond line represents a bond through the shared face of oxygen octahedra and –O– indicates corner-shared octahedra. A sequence of this kind has been found in the high temperature form of $BaMnO_3$.[7] This is the only example reported. The structure is shown in Fig. 8. The unit cell contains four AO_3 layers. It will be observed that the layer sequence portrayed in the left-hand figure consists of three spaces to the right and three to the left whereas in the $BaNiO_3$ structure it was two spaces to the right and two to the left.

The next sequence to be expected would be represented by a layer sequence of four spaces to the right and four to the left, shown in Fig. 9. This pattern results in a six-layer unit cell and is the structure of hexagonal barium titanate. Here we have two different environments for the B cations. One of the B cations lies in an octahedron of oxygens sharing opposite corners with adjacent octahedra, the other is in an octahedron of oxygens which shares one face with an adjacent octahedron and one corner with another octahedron. The latter situation is similar to that of the B cation in $BaMnO_3$. It seems plausible that this structure would be formed with two different kinds of B cations. It might be that the face-sharing corner-sharing tendency need be a property of only one of the B cations in the octahedra sharing faces.

(5) J. J. Lander, *Acta Cryst.*, **4**, 148 (1951).

(6) B. E. Gushee, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5601 (1957).

(7) A. Hardy, *Acta Cryst.*, **15**, 179 (1962).

(8) A. Clearfield, *ibid.*, **16**, 134 (1963).

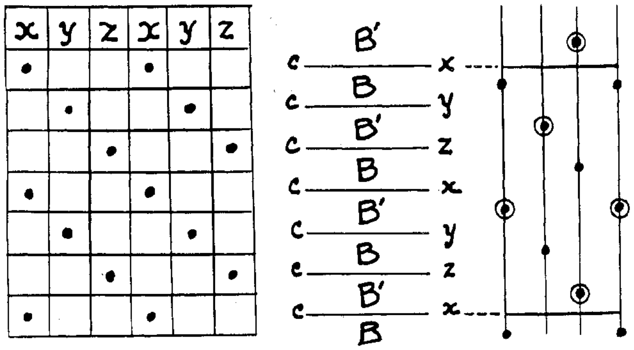


Fig. 5.—Six-layer ordered perovskite structure $A_2B'BO_6$.

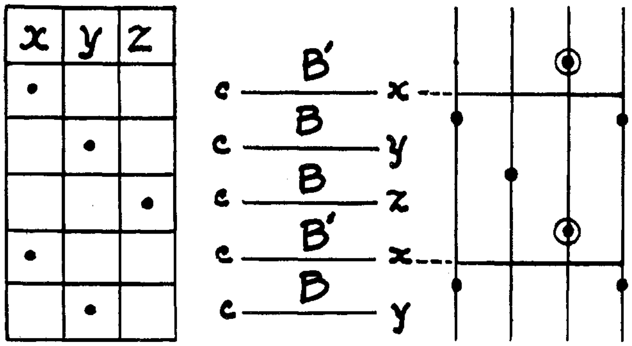


Fig. 6.—Three-layer ordered perovskite structure $A_3B'B_2O_9$.

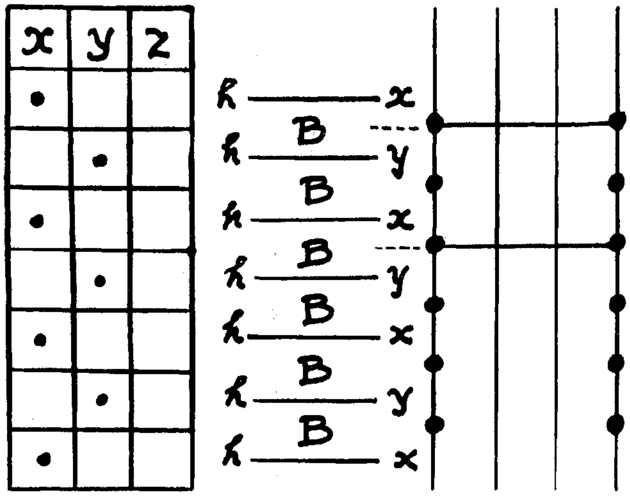


Fig. 7.—Hexagonal $BaNiO_3$.

Hexagonal barium titanate is formed only under conditions which either produce some trivalent titanium or introduce a foreign B cation.[9,10] When the phase has been formed, it is possible to oxidize the titanium to the tetravalent state without change of structure if the oxidation is carried out at a low enough temperature. Compounds which have been reported to have this structure are listed in Table III. The most favorable proportion of different kinds of B cations seems to be 1:2 but may also be 1:1. For example, Ba_2FeReO_6 has the ordered perovskite structure,

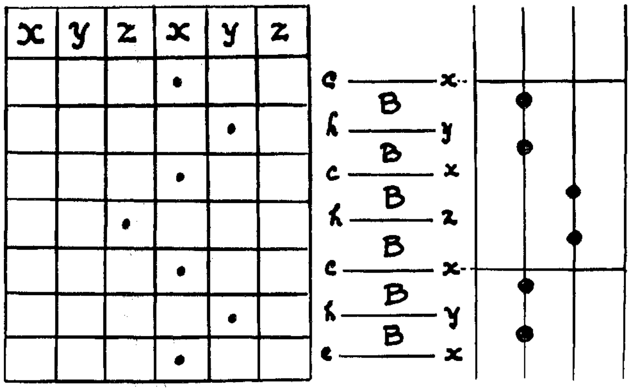


Fig. 8.—$BaMnO_3$ (high-temperature form).

but $Ba_3Fe_2ReO_9$ has the hexagonal barium titanate structure. On the other hand, almost all the compounds of composition $Ba_2CrB^VO_6$ have the hexagonal barium titanate structure.

TABLE III
COMPOUNDS WITH THE HEXAGONAL BARIUM TITANATE STRUCTURE

	a	*c*	Ref.
$BaTi^{III}_{0.48}Ti^{IV}_{0.52}O_{2.76}$	5.74	14.1	*a*
$Ba_3Ti_2IrO_9$	5.74	14.2	*a*
$Ba_3Fe_2ReO_9$	5.81	14.1	*b*
$Ba_3Cr_2ReO_9$	5.70	13.8	*b, c*
Ba_2MnOsO_6	5.82	14.2	*b, c*
Ba_2FeOsO_6	5.76	14.1	*b*
$Ba_3Cr_2MoO_9$	5.72	14.0	*d*
$Ba_3Cr_2WO_9$	5.75	14.3	*d*
Ba_2CrUO_6	5.83	14.4	*e*
Ba_2RhUO_6	5.84	14.9	*e*
$Ba_3Cr_2UO_9$	5.82	14.6	*e*
$Ba(Ti,V)O_3$	5.74	14.1	*a*
$Ba(Ti,Cr)O_3$	5.74	14.1	*a*
$Ba_3Ti_2MnO_9$	5.74	14.1	*a*
$Ba_3Ti_2FeO_9$	5.74	14.1	*a*
$Ba_3Ti_2CoO_9$	5.74	14.1	*a*
$Ba_3Ti_2RuO_9$	5.74	14.1	*a*
$Ba(Ti,Rh)O_3$	5.74	14.1	*a*
$BaTi_{0.9}Pt_{0.1}O_3$	5.74	14.1	*a*
$Ba_3Ti_2OsO_9$	5.76	14.3	*f*
$Ba(Fe,Ir)O_3$			*g*
Ba_2ScIrO_6	5.79	14.6	*f*
Ba_2InIrO_6	5.83	14.7	*f*
Ba_2ErIrO_6	5.91	14.6	*f*
Ba_2CrTaO_6			*f*
Ba_2CoOsO_6	5.74	14.1	*b, f*
Ba_2NiOsO_6	5.75	14.1	*b, f*
Ba_2FeSbO_6	5.76	14.5	*f*
Ba_2RhTaO_6	5.75	14.5	*f*
$Ba_3Cr_2ReO_9$	5.70	13.8	*b, c*
Ba_2CrOsO_6			*f*

[a] Reference 9. [b] A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, 1, 245 (1962). [c] R. Ward, *ibid.*, 1, 723 (1962). [d] F. K. Patterson, C. W. Moeller, and R. Ward, *ibid.*, 2, 196 (1963). [e] A. W. Sleight and R. Ward, *ibid.*, 1, 790 (1962). [f] A. W. Sleight, Ph.D. Thesis, University of Connecticut, 1963. [g] A. Paton, M.S. Thesis, University of Connecticut, 1962.

It is noteworthy that all of the ternary oxides which have structures involving face-sharing of filled octahedra have barium as the A cation. (An unpublished report by Paul Braun indicates that $SrMnO_3$ has the $BaMnO_3$ structure.) Two possible explanations may

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(9) J. G. Dickinson, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **83**, 3026 (1961).
(10) O. Spitzbergen, Doctoral Thesis, U. of Leyden, 1962.

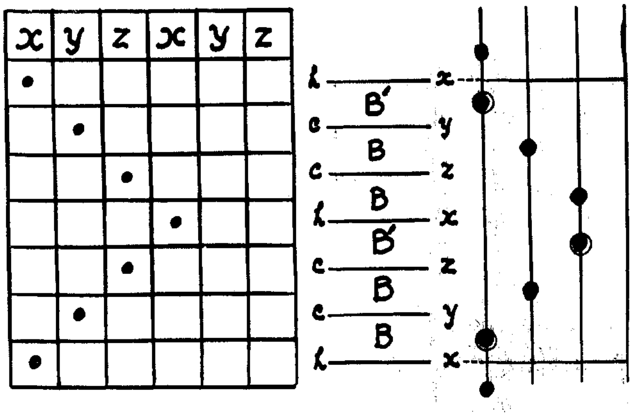

Fig. 9.—Hexagonal barium titanate structure $Ba_3B_2B'O_9$.

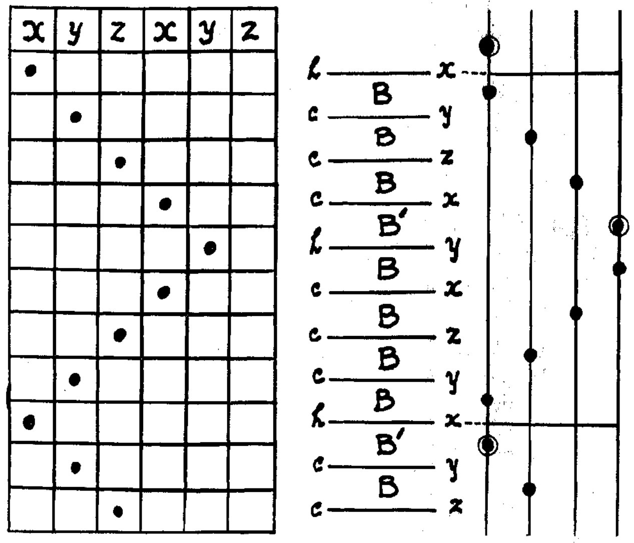

Fig. 10.—Eight-layer structure (unknown) $Ba_4B_3B'O_{12}$ involving metal–metal bonds.

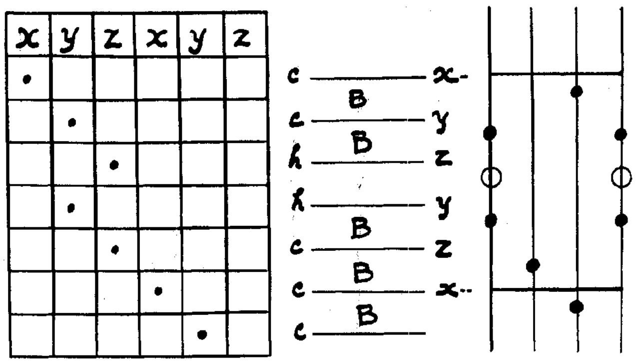

Fig. 11.—The $Ba_5Ta_4O_{15}$ structure.

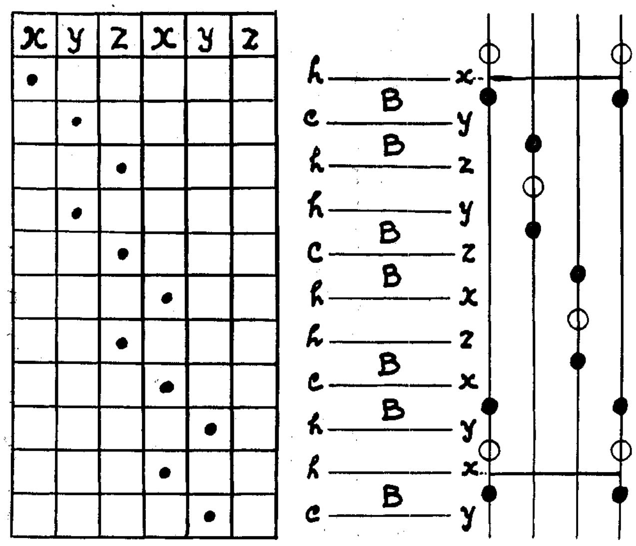

Fig. 12.—Nine-layer structure (unknown) $A_9B_6O_{27}$ involving vacant octahedral sites.

be offered. One is that the large A cation has very little polarizing action on the oxide ion, which is then more subject to having its filled orbitals overlap with empty d-orbitals of the B cation. The other suggestion is that the larger A cation causes a greater separation of the AO_3 layers—enough to permit the presence of two cations in spite of the repulsive forces and thus enable them to form a bond. It is interesting to note that $CsMnF_3$ has the hexagonal barium titanate structure whereas $KMnF_3$ has the perovskite structure.

There is apparently some need for d-orbitals and for d-electrons in at least one of the metal atoms occupying adjacent octahedral sites in hexagonally close-packed AO_3 layers. The d-electrons do not appear to be required with the more highly polarizable sulfide ions in the compound $BaTiS_3$.

The next extension of the idea of periodic switching from close packed cubic to close packed hexagonal arrangement of the AO_3 layers calls for the structure presented in Fig. 10. This would be an eight-layer hexagonal unit cell. Among the eight B cations, only two would have to be of the face-sharing type provided the other type had available empty d-orbitals. Such a compound might be $Ba_4MnSn_3O_{12}$ or $Ba_4MnTi_3O_{12}$, but the likelihood of achieving the necessary order instead of two separate phases seems quite remote. Achievement of order obtainable in the case of the hexagonal barium titanate structure by simple alternation of the B cations is not possible with this structure. Neither does it appear reasonable to expect ordering through large charge differences in the B cations. We might envisage a succession of B cations such as Sb^{V}, In^{III}, Ta^{V}, Cr^{III}, the first two ions being in the corner-sharing octahedra, the other two in the face-sharing octahedra, but again the more probable product would be a mixture of cubic Ba_2SbInO_6 and hexagonal Ba_2TaCrO_6.

It can be seen that a practical limit may be placed on the extension of this simple scheme.

Vacancies in Octahedral Sites.—Another development based on close-packed AO_3 layers occurs when the oxidation state of the B cation is sufficiently high to require vacant oxygen octahedra. B cation vacancies do not seem to occur in oxides of the perovskite type. Some halogen compounds such as K_2PtCl_6 may be described as perovskite structures with B cations missing from alternate corners of the cube.[11] Such an arrangement seems to be possible only when a discrete ion

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(11) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford at the Clarendon Press, p. 369; see also pp. 112–129 and 374 ff. for a discussion of close packing.

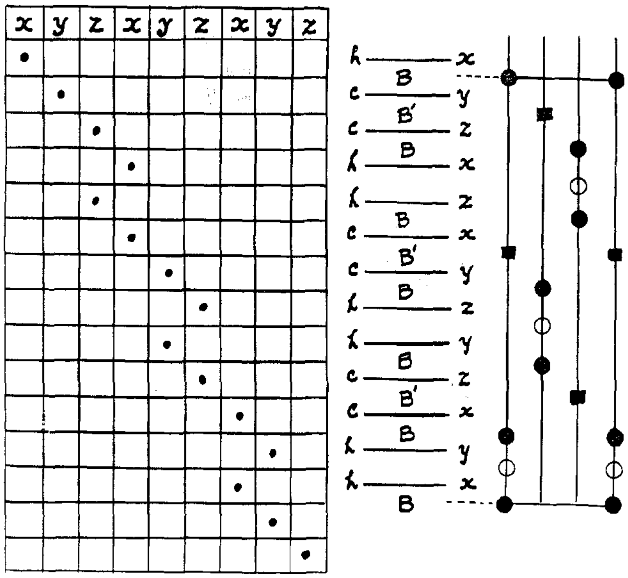

Fig. 13.—$A_{12}B_6B'_3O_{36}$.

exists in the crystal. Analogous compounds among the oxides have not been reported. A compound such as La_2ReO_6 or La_2WO_6 is not a likely candidate, for La_2MoO_6 has been assigned a structure in which the molybdenum atoms are in tetrahedral coordination with oxygen.[12] B cation vacancies in oxides, however, can be brought about by the introduction of hexagonal close packing.

The first instance of this structure in the ternary oxides was found with the compound $Ba_5Ta_4O_{15}$.[13] The structure described in Fig. 11 is shown to be a five-layer sequence. The vacant octahedron shares opposite faces with occupied octahedra which in turn share corners with the octahedra in the next layers. The pattern of the layer sequence is clearly shown at the left of Fig. 11; three cubic close packed layers followed by two close packed hexagonal layers. One might assume that the unfavorable charge balance of the oxygens in the cubic close packed layers together with the high repulsive forces between the highly charged B cations results in the creation of a layer of vacant octahedral sites. We should expect this structure only with B cations of high valence. It is interesting to note that compounds of this type containing niobium or tantalum are readily obtained with oxygen deficiencies. A single crystal of composition $Ba_5Ta_4O_{13}$ (deep blue in color) was oxidized without change in structure to the colorless $Ba_5Ta_4O_{15}$. The structure is a fairly stable one. The ordered perovskite compound $Ba_3SrTa_2O_9$ is converted at high temperatures to $(Ba,Sr)_5Ta_4O_{15}$.[3]

If we adopt the idea that B cation vacancies may be introduced by having two successive hexagonal (h) layers sandwiched between layers of cubic close packing (c), other structures can be pictured. One cubic close packed layer between the pairs of close packed hexagonal layers leads to the structure shown in Fig. 12. The repeat unit with this arrangement is a nine-layer structure. No example of this has been found so far among the oxides. A possible candidate would be $Sr_3U^{VI}{}_2O_9$ but the structure of this substance has not yet been determined.

Next should come the structure with two cubic close packed layers interposed between the pairs of close packed hexagonal layers. It is shown in Fig. 13. The unit cell for this structure is a twelve-layer sequence. The empirical formula for such a compound is $A_4B_3O_{12}$. Compounds which apparently correspond to this structure have been formed by heating rhenium compounds $A^{II}{}_2Re^{VI}B^{II}O_6$ in air. The rhenium is oxidized to the heptavalent state and some of the B oxide is lost giving phases of composition $A^{II}{}_4Re^{VII}{}_2B^{II}O_{12}$. The compounds may also be formed by heating appropriate mixtures of the binary oxides or of the metals in air. The compound $Sr_4Re_2SrO_{12}$, for example, may be prepared by heating a mixture of strontium oxide and rhenium metal in air at 1200°.

The X-ray powder patterns of compounds $Ba_4Re_2B^{II}O_{12}$ are indeed indexable using hexagonal cells corresponding to twelve-layer repeat distances. Preliminary intensity calculations for the compound with $B^{II} = Co$ are also in agreement with a structure based on the twelve-layer model.

It should be pointed out that all of these compounds involving vacant oxygen octahedra may be prepared with strontium as the A cation just as well as with barium.

Other possible sequences of layers can be suggested readily. They involve either an increase in the number of cubic close packed layers interposed between the pairs of hexagonal close packed layers or the adoption of a varied sequence such as –hhchhcc– or –hhcchhcccc. It is our belief that such periodicity would be difficult to achieve experimentally. Awkward stoichiometries are encountered, more than two different kinds of B cations may be required, or the influence of a vacancy has to be spread too far to be effective.

Alternative Scheme for Predicting Many-Layer Sequences.—If we consider the h and c description for stacking we note that when the number of layers (N) is 2, the description is simply h; when $N = 3$, the description is simply c; when $N = 4$, the description is hc. For $N = 5$, the description is ccchh. For $N = 6$, there are two possibilities: hcc and chhhch. The one observed, in hexagonal $BaTiO_3$, is the simpler one, hcc. In fact, the longest description required for the compounds discussed is the five-symbol description for $N = 5$.

In general, one might expect that the most likely sequences would be those with the simplest descriptions in terms of hexagonal and cubic stacking, particularly if the rather uncommon repetition of hexagonal layers leading to strings of face-shared octahedra is avoided.

When N is a multiple of three, rhombohedral lattices are possible ($N = 6$ is an exception).[14] For these

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rhombohedral cases, the h, c description requires only $^1/_3N$ symbols. Thus the nine-layer rhombohedral case may be described simply as chh; the twelve-layer rhombohedral case as cchh. In this way one can see the basic simplicity of these patterns, even though N is large, and the correspondingly simple patterns of the corner and face sharing octahedra which they produce. As a consequence of these simple stacking sequence patterns, face sharing of octahedra containing cations can be avoided altogether through simple patterns of octahedral site vacancies. Alternatively, simple patterns of cation substitution can put different kinds of central cations in the octahedra sharing faces and/or corners.

Both the nine-layer and the twelve-layer models proposed have primitive rhombohedral lattices. The reflection absences noted for $Ba_4Re_2B^{II}O_{12}$ compounds very nearly correspond to the rhombohedral lattice requirement, and the atomic positions used for a trial structure are in space group 166, $R\bar{3}m$.

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Hydrogen Bonding to Chloro and Bromo Complexes of Uranium(IV)[1]

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Spectrophotometric studies of nonaqueous solutions of U(IV) in the presence and absence of hydrogen bond donors are used to demonstrate the ability of the UCl_6^{-2} and UBr_6^{-2} complexes to form hydrogen bonds with primary, secondary, and tertiary alkylammonium ions and with hydronium ion. This hydrogen bonding partially distorts the octahedral field around the U^{+4} ion in the UCl_6^{-2} and UBr_6^{-2} complexes and thereby allows the normally forbidden electric dipole induced internal 5f electronic transitions to occur. The occurrence of such transitions in the hexachlorouranate(IV) complex in anion-exchange resins indicates distortion of the complex, most probably due to hydrogen bonding.

Hydrogen bonding of hydronium ion and primary, secondary, and tertiary alkylammonium ions to the complexes $MO_2Cl_4^{-2}$ where M is U(VI), Np(VI), or Pu(VI) has been demonstrated.[2] These complexes contain oxygen as well as chloride as ligands and it was not determined whether this hydrogen bonding was through the chloride or the oxygen of the complex. Thus it was not possible to predict whether such hydrogen bonding might be expected with simple chloro complexes. Because of this the UCl_6^{-2} system was examined for evidence of hydrogen bonding.

The hexachlorouranate(IV) complex has been shown to be the species absorbed by anion-exchange resins[3] and extracted into tertiary alkylammonium extractants.[4] Both of the systems are ones in which hydrogen bonding occurs in the case of the $MO_2Cl_4^{-2}$ complexes.[2] Careful examination of the absorption spectra of U(IV) chloride in anion-exchange resins[3] and in tertiary ammonium extracts[4] showed that there are distinct differences between these spectra and the spectra of $[(C_2H_5)_4N]_2UCl_6$ in nitromethane in which no hydrogen-bond donor is present. The visible and near-infrared absorption spectrum of UCl_6^{-2} has been extensively interpreted by Satten and co-workers.[5,6] The UBr_6^{-2} complex has been prepared and its absorption spectrum interpreted.[7-9]

In this work the existence of hydrogen bonding of the UCl_6^{-2} complex to a variety of hydrogen-bond donors will be shown and the effect of this hydrogen bonding on the absorption spectrum will be discussed. Hydrogen bonding to the complex UBr_6^{-2} will also be demonstrated.

Experimental

Materials Used.—Alkylammonium chlorides were prepared and purified as before.[2] $[(C_2H_5)_4N]_2UCl_6$ and $[(C_2H_5)_4N]_2UBr_6$ were also prepared by the methods used previously.[8,9] Secondary and tertiary alkylammonium perchlorates were prepared by partial neutralization of the free amines (obtained from Eastman) with concentrated perchloric acid. Water and excess amine were removed by vacuum drying at 60°. No further purification of these slightly colored salts was carried out. (Note: No evaluation of the stability of these alkylammonium perchlorates was made and they were prepared and handled only in small quantities.) Triethylammonium iodide was prepared by neutralization of the free amine with concentrated HI. It was recrystallized from acetone until it was colorless. The preparation of the anhydrous UCl_4 used is discussed elsewhere.[10] Solutions of U(IV) chloride in organic solvents containing HCl were prepared by dissolving uranium metal directly in the HCl-containing solvent. $[(C_6H_5)_3PH]_2UCl_6$ was prepared by a slight modification of the previous method.[7,8] An acetone solution of triphenylphosphine saturated with HCl was added to a solution prepared by dissolving uranium metal directly in HCl–acetone. The resultant crystals were washed with acetone and vacuum dried at room temperature. Nitromethane and acetonitrile were Eastman Spectro Grade and acetone was C.P. grade.

Spectrophotometric Measurements.—Spectrophotometric measurements were made with a Cary Model 14 recording spec-

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