QUARTERLY REVIEWS

THE STRUCTURES OF METALLIC OXIDES

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In this Review we shall be largely concerned with the atomic structures of crystalline oxides as determined by the *X*-ray diffraction method. The chemist normally deals only with finite groups of atoms—molecules and complex ions—and classical stereochemistry is therefore the study of the spatial arrangement of atoms in such finite groups. One result of the development of *X*-ray crystallography has been the extension of stereochemistry to include also the infinite arrays of atoms constituting crystals. For a proper understanding of the geometry of crystal structures it is necessary to appreciate an essential difference between the stereochemistry of finite and of infinite groups of atoms. In a finite molecule such as AX_3 (*a*), there are three X atoms attached to A. The same empirical composition can be realised in the bridged molecule A_2X_6 (*b*) or in the cyclic molecule A_3X_9(*c*), in both of which there are four X atoms attached to each A atom. In a crystal there are clearly many more possibilities for a compound with the empirical formula AX_3, for the only requirement is that the ratio of the numbers of X to A atoms is 3 : 1, and the systems of atoms can extend indefinitely in one, two, or three dimensions. This can be realised in infinite chain molecules such as

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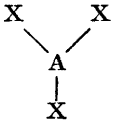
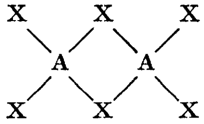


(*b.*)



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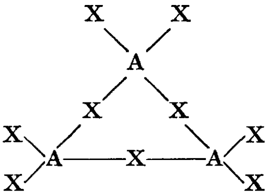

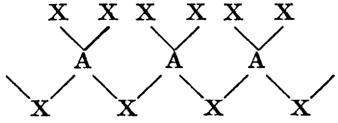

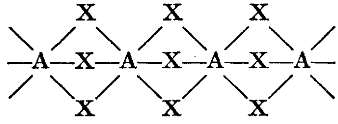

or in layers or 3-dimensional arrays of atoms. It will be apparent that there is no simple relation between the empirical formula AX_3 and the numbers of X atoms attached to each A atom. In crystals all these types of grouping are found, from finite molecules to infinite 3-dimensional arrays in which there is no reason to distinguish any finite molecules, and as in the simple example AX_3 so in more complex compounds the empirical formula does not necessarily give any indication of the spatial arrangement of the atoms. In particular, similarity in formula type is no indication of similarity in structure, as shown by the following examples:

ABO_3.	Type of complex ion.	Number of O atoms attached to a B atom.
$CaCO_3$	Finite $CO_3{}^{2-}$ ion	3
$CaSiO_3$	Cyclic $Si_3O_9{}^{6-}$	4
$MgSiO_3$	Infinite chain ion	4
$CaTiO_3$	No complex ion (perovskite structure, Fig. 8)	6

It is important to remember that if the crystal contains extended arrangements of atoms (*i.e.*, *not* finite molecules or complex ions) then these must break down when the crystal is vaporised or dissolved. The relations between the structures of a substance in the different states of aggregation form an important part of this broader structural chemistry which has developed in recent years, and this aspect of the subject should be borne in mind when considering the relevance of the crystal structure to a particular chemical problem. It would not be possible to describe, still less to illustrate, all the known oxide structures in the space of this article. Instead, we shall attempt a broad outline of our present knowledge of this field, with particular reference to certain aspects of oxide structures which are of special interest from the chemical standpoint. We shall deal only with true oxides, *i.e.*, those containing discrete oxygen atoms or O^{2-} ions, and exclude the small number of peroxides and superoxides which contain respectively $O_2{}^{2-}$ or $O_2{}^{-}$ ions (*e.g.*, Na_2O_2, KO_2).

Survey of Oxide Structures.—Oxides range from the essentially ionic compounds of the more electropositive elements to the molecular oxides of carbon, nitrogen, sulphur, and the halogens. Apart from fluorine, oxygen is the most electronegative of the elements, and therefore in the majority of the metallic oxides the bonds are largely ionic in character. The structures of such oxides are generally simple, the arrangement of O^{2-} ions around a metal ion being the most symmetrical possible, namely, at the apices of an equilateral triangle, tetrahedron, octahedron, or cube for 3-, 4-, 6-, or 8-co-ordination respectively. The co-ordination numbers of the metal and oxygen ions are determined by their relative sizes. For example, in a simple ionic crystal AB the co-ordination number (which must be the same for both ions) is limited to the greatest number of the larger ions which can be packed around one of the smaller. As will be seen from Table I, most metal ions are appreciably smaller than the oxygen ion, and the smallest (*e.g.*, Be^{2+}) are found surrounded by only 4 oxygen ions. Those of intermediate size, with radii between 0·5 and 1·0 A. approximately, are 6-co-ordinated, while the larger ions exhibit co-ordination numbers up to 12.

We shall describe two other groups of metallic oxides, both small compared with the first group. In the oxides of a number of less electropositive metals the bonds have more covalent character, and the number and

TABLE I

The radii of some metal ions referred to $O^{2-} = 1{\cdot}40$ A.

+ 1.	+ 2.	+ 3.	+ 4.					
Li 0·60 Na 0·95	Be 0·31 Mg 0·65	Al 0·50	(Si) 0·41	Mn^{2+} 0·80 Ti^{3+} 0·69	Fe^{2+} 0·75 V^{3+} 0·66	Co^{2+} 0·72 Cr^{3+} 0·64	Ni^{2+} 0·70 Mn^{3+} 0·62	Fe^{3+} 0·60
K 1·33 Rb 1·48 Cs 1·69	Ca 0·99 Sr 1·13 Ba 1·35	Sc 0·81 Y 0·93 La 1·15	Ti 0·68 Zr 0·80 Ce 1·01	Sn^{4+} 0·71	Pb^{4+} 0·84 Tl^{3+} 0·95	Pb^{2+} 1·21 Tl^{+} 1·44		

arrangement of bonds from a metal atom is the same as in covalent molecules and complex ions formed by the metal. This group includes PdO, PtO, and CuO, all with closely related structures. We shall also include here PbO and SnO, though their structures cannot be related to the stereochemistry of Pb^{II} and Sn^{II} since nothing is known of the structures of simple molecules in which the same covalency (4) is exhibited. Our third group includes the oxides of the "semi-metals", arsenic, antimony, and selenium, where we find molecular or chain structures. It will be appreciated that any broad classification of oxides in terms of the Periodic Classification is difficult because of the very different properties of an element in different valency states. For example, the elements of the later A subgroups are much more electronegative in their higher valency states (*e.g.*, V^{V}, Cr^{VI}, Mn^{VII}) than in the lower, so that while the structural chemistry of the oxy-compounds of quinquevalent vanadium is quite similar to that of quinquevalent phosphorus, the structures of V_2O_3 and VO_2 are the same as those of the ionic sesquioxides and dioxides of many other transition elements. Also, whereas the oxides of some B sub-group elements are covalent compounds (*e.g.*, As_4O_6, SeO_2), the lower oxides of the more metallic members of the later B sub-groups have typical ionic structures, as in the case of TeO_2 with the rutile structure.

Oxides containing metal atoms of more than one kind often have structures closely related to those of simple metallic oxides. We shall describe the structures of some complex oxides later. In recent years it has been found that a number of oxides are not quite such simple compounds as they once appeared to be. First, the actual structure is in some cases not the simple structure first assigned to the oxide but a slightly distorted version of the simpler, more symmetrical structure. Examples are MoO_2 and WO_2 with distorted versions of the rutile structure, and NiO with a slightly deformed rock-salt structure. The reasons for small distortions from a simpler structure are generally not known, and these structures present an interesting problem. A related phenomenon is the distorted version of the PdO structure adopted by CuO. Secondly, a number of oxides are non-stoicheiometric compounds; we shall refer later to FeO as an example of this type of oxide. A third point of interest is that it is apparently impossible to prepare certain oxides in a state of purity if they are made by calcining a hydroxide or oxy-hydroxide. A possible explanation of this difficulty is suggested later in connection with the oxides of iron and manganese.

Ionic Oxide Structures.—Oxides MO. The structure most commonly found is the rock-salt structure, in which M^{2+} and O^{2-} ions are 6-co-ordinated. Examples include: MgO, CaO, SrO, BaO, CdO, VO, MnO, FeO, and CoO. It has recently been found [1] that, whereas FeO and CoO have the normal rock-salt structure, NiO adopts a very slightly distorted (rhombohedral) variant of this structure. In the 4-co-ordinated structures of BeO (wurtzite structure) and ZnO (wurtzite and zinc blende structures) the metal-oxygen bonds are probably rather more covalent in character than in MgO and the alkaline-earth oxides.

Oxides MO_2 *and* M_2O. The former adopt either the rutile or the fluorite structure, according to the size of M^{4+}, with respectively octahedral and cubic co-ordination of the metal ions. Dioxides with the rutile structure include SnO_2, TiO_2, VO_2, RuO_2, MnO_2, and PbO_2, and with the fluorite structure, ThO_2, CeO_2, and UO_2 (larger M^{4+} ions). The alkali-metal oxides Li_2O, Na_2O, K_2O, and Rb_2O have the anti-fluorite structure, so called because the M^+ ions occupy the F^- positions and the O^{2-} ions the Ca^{2+} positions of the CaF_2 structure. Cs_2O has been assigned the $CdCl_2$ (layer) structure,[2] but the evidence was only a powder photograph, and it would appear desirable to check this structure.

Oxides MO_3. The very simple structure of ReO_3 is illustrated later (Fig. 8) in connection with the structures of complex oxides ABO_3. Of the other Group VIA trioxides, WO_3 and CrO_3 have slightly deformed versions of the ReO_3 structure, while MoO_3 has a quite different (layer) structure.

Oxides M_2O_3. The structures most commonly found for metallic "sesquioxides" are the corundum structure (α-Al_2O_3, α-Fe_2O_3, Cr_2O_3, Ti_2O_3, V_2O_3, etc.) and the so-called A and C rare-earth sesquioxide structures. The corundum structure consists of close-packed oxygen atoms in which the metal ions occupy positions of octahedral co-ordination.

Oxides M_3O_4. A few metals form oxides M_3O_4, which necessarily contain the element in two different valency states. For this reason some of these oxides are structurally similar to complex oxides—compare the isomorphism of Pb_3O_4 with $ZnSb_2O_4$. The structures of Pb_3O_4 and Fe_3O_4 are mentioned later; others include Co_3O_4 and Mn_3O_4, and a compound which may be Pt_3O_4 has been obtained by prolonged oxidation of a platinum wire.[3]

The Oxides of Cu, Ag, Pd, Pt, Sn, *and* Pb.—We group together the oxides

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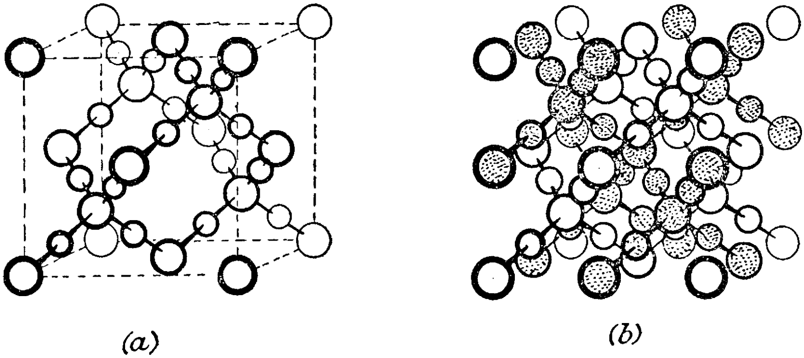
[1] H. P. Rooksby, *Nature*, 1943, **152**, 304.
[2] A. Helms and W. Klemm, *Z. anorg. Chem.*, 1939, **242**, 33.
[3] E. E. Galloni and A. E. Roffo, *J. Chem. Physics*, 1941, **9**, 875.

of these less electropositive metals because, with the exception of SnO_2 and PbO_2 which are normal ionic oxides, they have structures of low co-ordination numbers in which the bonds have considerable covalent nature. The structures therefore illustrate the stereochemistry of these atoms in certain valency states.

The isomorphous Cu_2O and Ag_2O have a rather simple cubic structure in which the metal atoms form two collinear bonds and the oxygen atoms four tetrahedral bonds (Fig. 1*). This structure is unique among crystal structures in that it consists of two completely interpenetrating and identical frameworks which are not cross-connected by any primary (Cu–O) bonds. Each framework is in fact of exactly the same form as the silicon–oxygen framework of the low-temperature modification of cristobalite, if the oxygen atoms are placed midway along the lines joining the silicon atoms. (Actually they lie slightly off these lines.) Instead of the structure consisting of one such cage-work, as in cristobalite, there are two in Cu_2O displaced relatively to one another by the length of the edge of the unit cell. The only other comparable type of crystal structure known at present is that recently found for β-quinol,[4] though here each framework consists of molecules held together by O–H–O bonds.


(a)

(b)

Fig. 1

(*a*) *Framework of* Cu *and* O *atoms* (*larger circles*). (*b*) *Structure of crystalline* Cu_2O, *consisting of two interpenetrating frameworks of type* (*a*).

In the isomorphous PdO and PtO, illustrated in Fig. 2(*b*), the metal atoms form four coplanar bonds, as in many molecules and complex ions containing Pd^{II} and Pt^{II}. The oxygen atoms form the usual tetrahedral bonds. The structure of CuO (Fig. 2*a*) is of the same general type, with Cu^{II} forming four coplanar bonds, but of much lower symmetry. Again, the structure of PdS is very similar to that of PtS but less symmetrical, so that we have here further examples of minor distortions from more symmetrical structures for which no explanations are as yet available.

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[4] D. E. Palin and H. M. Powell, *J.*, 1947, 208.

* Figs. 2, 3, 5, 6, 7, and 8 are from Wells's " Structural Inorganic Chemistry ", Clarendon Press, 1945.

The monoxides SnO and PbO (tetragonal form) have a rather extraordinary layer structure in which a metal atom is bonded to four oxygen atoms which are arranged in a square to one side of it. If we formulate PbO as a covalent crystal, the Pb atom has the valency group $(2, \bar{6}, \bar{2})$, and a reasonable explanation of the four pyramidal bonds is that the inert pair of 6*s* electrons occupies the apex of the tetragonal pyramid (Fig. 3). It will be noticed that adjacent layers in this structure are held together by bonds between Pb atoms, and the lead oxides are clearly not normal oxides, as is shown, for example, by the brilliant colours of yellow PbO (rhombic form), red PbO (tetragonal form), and red Pb_3O_4—compare also the brilliant metallic lustre of galena (PbS) and the colours of certain other metallic sulphides.

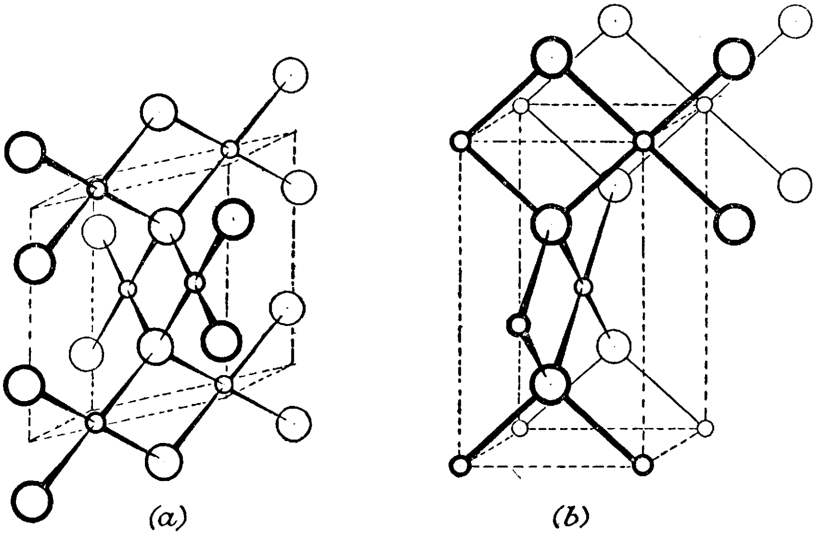

FIG. 2

The crystal structures of (*a*) CuO, *and* (*b*) PdO *and* PtO. *The small circles represent metal atoms.*

Although the existence of three oxides of lead, PbO, Pb_3O_4, and PbO_2, seems to have been universally recognised for a long time, there is far less agreement concerning the compositions, or even the existence, of various other oxides such as Pb_2O_3, Pb_5O_8, etc. Since the oxides of lead are to some extent interconvertible (by heating in air or by oxidation) mixtures are often obtained. The structure of the red form of PbO has already been described. So far it has proved impossible to deduce the positions of the oxygen atoms in the yellow orthorhombic PbO directly from the intensities of the *X*-ray reflexions, owing to the preponderating effect of the lead atoms, but a reasonable structure has been proposed by A. Byström.[5] The lead atoms are arranged in layers, and between every other pair of

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[5] *Arkiv Kemi, Min. Geol.*, 1943, **17***B*, No. 8.

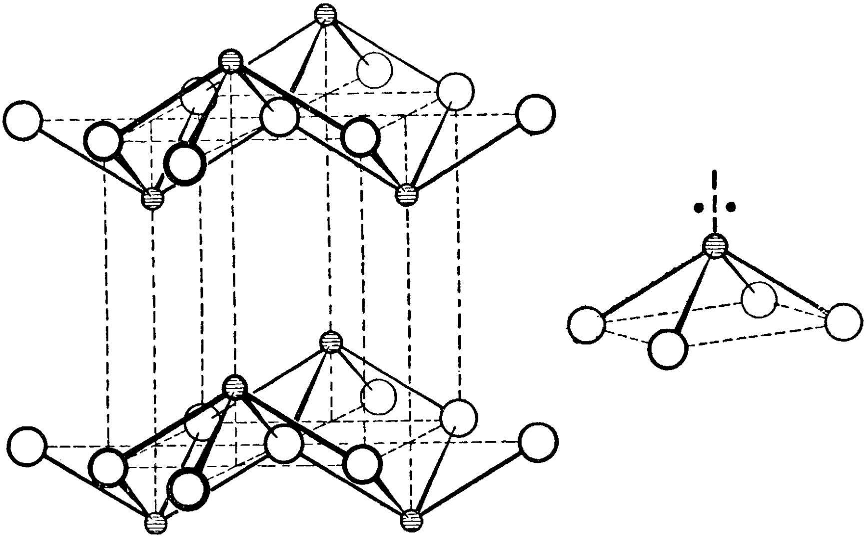


FIG. 3

The crystal structure of PbO *(tetragonal form). The small shaded circles represent metal atoms. The arrangement of bonds from a metal atom is shown at the right, where the two dots represent the "inert pair" of electrons.*

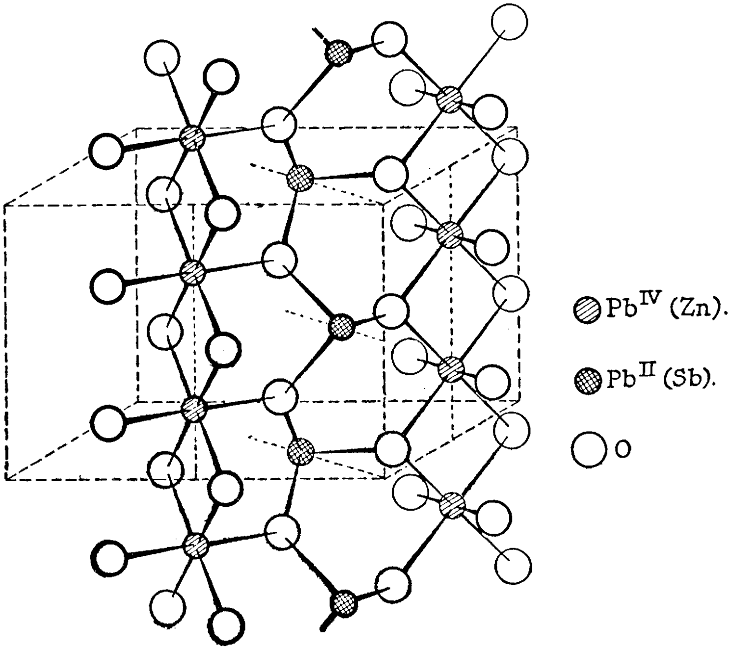


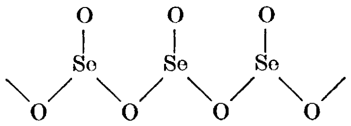
FIG. 4

The crystal structure of Pb_3O_4 *(and* $ZnSb_2O_4$*), showing the strings of* $Pb^{IV}O_6$ *octahedra joined by* $Pb^{II}O_3$ *pyramids.*

lead layers there is a puckered layer of oxygen atoms. The Pb–O bond lengths and the angles between these bonds are very similar to those found for the Pb^{II} atoms in Pb_3O_4. The structure of Pb_3O_4 [6, 7, 8] is illustrated in Fig. 4. It consists of chains of $Pb^{IV}O_6$ octahedra sharing opposite edges, these chains being linked together through the Pb^{II} atoms, each of which forms three pyramidal bonds to its nearest oxygen neighbours.

As regards other oxides of lead the position is less clear, for a number of studies have been made of the oxidation of PbO and of the decomposition products of PbO_2 but the results are by no means in agreement. According to M. le Blanc and E. Eberius [9] the phases are: PbO, the composition of which can vary between PbO and $PbO_{1\cdot10}$ without change of structure, a red form of Pb_3O_4 of constant composition, a black oxide of composition $PbO_{1\cdot13}$—$PbO_{1\cdot66}$, and PbO_2 which can lose oxygen until the composition $PbO_{1\cdot66}$ is reached. Other investigators have claimed that the black "Pb_3O_4" is a mixture of Pb_5O_8 and PbO_x [10] or that there is an oxide Pb_7O_{11}.[11] A recent *X*-ray study [12] of the decomposition of PbO_2 in air has indicated the existence of phases β-PbO_x (with composition close to Pb_2O_3) and α-PbO_x (probably corresponding to the Pb_5O_8 of Clark and Rowan and the Pb_7O_{11} of Holtermann). The wide composition range of PbO_2 is not confirmed.

The Oxides of Se, Te, As, Sb, *and* Bi.—Of the oxides of selenium and tellurium, SeO_2 and TeO_2 have been studied by the *X*-ray method. The former consists of infinite chains of the type



while the latter forms ionic crystals with either the rutile structure or a distorted version of the structure of brookite, another of the polymorphic forms of TiO_2. The oxides SO_2, SeO_2, and TeO_2 form an interesting series, from the molecular SO_2 through SeO_2—with infinite linear molecules—to the ionic TeO_2. In the case of arsenic and antimony only the structures of the lower oxides are known, As_2O_3, Sb_2O_3, and Sb_2O_4. It seems likely that of the tetroxides of the VB sub-group elements only Sb_2O_4 is a definite compound; its structure is mentioned later. Unlike P_2O_5, the pentoxides of arsenic and antimony cannot be prepared pure by the direct oxidation of the elements, for they decompose at high temperatures with loss of oxygen. They are therefore prepared by the cautious "dehydration" of H_3AsO_4 or "antimonic acid" (probably colloidal hydrated Sb_2O_5) respec-

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[6] M. Straumanis, *Z. physikal. Chem.*, 1942, *B*, **52**, 127.
[7] S. T. Gross, *J. Amer. Chem. Soc.*, 1943, **65**, 1107.
[8] A. Byström and A. Westgren, *Arkiv Kemi, Min. Geol.*, 1943, **16***B*, No. 14.
[9] *Z. physikal. Chem.*, 1932, *A*, **160**, 69.
[10] G. L. Clark and J. Rowan, *J. Amer. Chem. Soc.*, 1941, **63**, 1305.
[11] C. Holtermann and P. Lafitte, *Compt. rend.*, 1937, **204**, 1813.
[12] A. Byström, *Arkiv Kemi, Min. Geol.*, 1945, **20***A*, No. 11.

tively. Bismuth pentoxide can be prepared by the oxidation of the trioxide in solution or by fusion with potassium chlorate, but it appears to be a rather ill-defined compound often containing alkali and water.

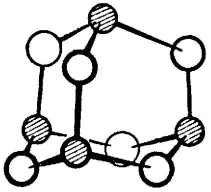
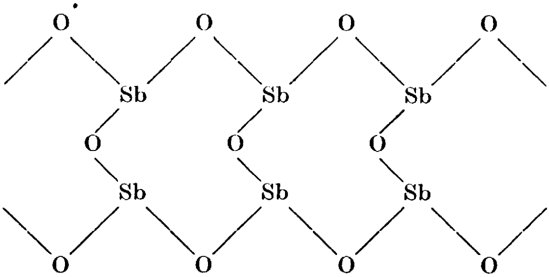


FIG. 5

Molecule of As_4O_6 *(or* Sb_4O_6*). The shaded circles represent metal atoms.*

Each of the trioxides exists in at least two polymorphic modifications. Vaporisation of arsenic and antimony trioxides gives molecules As_4O_6 and Sb_4O_6 which break down to the simpler M_2O_3 molecules only at higher temperatures. The structure of the As_4O_6 molecule in the vapour state has been shown, by electron diffraction, to be similar to that of P_4O_6 (Fig. 5). In the cubic forms of these trioxides there are molecules of the same type.[13] The structure of the low-temperature form of As_2O_3, stable below — 13°, has not been determined. The second form of antimony trioxide, the mineral valentinite, has quite a different type of structure from the cubic form. Instead of finite molecules, Sb_4O_6, there are infinite double chains of the type



in which Sb^{III} forms the usual three pyramidal bonds, with bond angles of about 90°.

A rather complex structure has been proposed [14] for the low-temperature (α-) form of Bi_2O_3, but there still appears to be some doubt about the number and structures of the high-temperature forms of this oxide. Some of the confusion concerning the polymorphism of Bi_2O_3 is probably due to the fact that this compound (like certain other oxides, *e.g.*, alumina) is very easily contaminated, in this case by Si, Fe, etc. Sillén [15] has shown that fusion for a short time in a porcelain crucible gives a body-centred cubic phase with the probable composition $Si_2Bi_{24}O_{40}$, and similar phases containing iron or aluminium (possibly $M_2^{III}Bi_{24}O_{39}$) have also been prepared. If Bi_2O_3 is fused for a long time in a porcelain crucible, a simple cubic phase is obtained which apparently has the structure shown in Fig. 6(*a*) stabilised by a small amount of impurity. This structure is the same as that of Mn_2O_3, and it is closely related to the fluorite structure, which is shown

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[13] K. E. Almin and A. Westgren, *ibid.*, 1942, **15***B*, No. 22.

[14] L. G. Sillén, *Z. Krist.*, 1941, **103**, 274.

[15] Diss., Stockholm, 1940.

in the same orientation in Fig. 6(*b*). Removal of one-quarter of the anions (those shown as dotted circles) from the unit cell of the latter leaves the arrangement shown at (*a*). This structure is closely related to the (molecular) structure of the cubic forms of arsenic and antimony trioxides. If we imagine the metal atoms and the shaded oxygen atoms to be drawn in a little towards the centre of the cube, the structure becomes that of As_4O_6 and Sb_4O_6, containing discrete molecules.

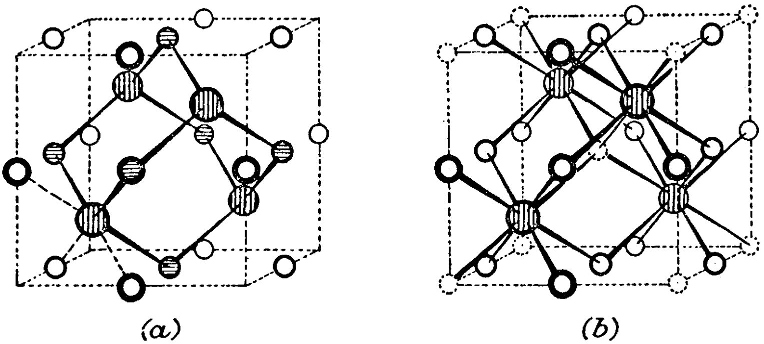
(*a*) (*b*)

FIG. 6

The crystal structures of (*a*) Bi_2O_3 *and* (*b*) CaF_2. *Metal atoms are shaded vertically.*

Complex Oxides

Compounds $A_aB_b \ldots O_n$, containing two or more different kinds of atom in addition to oxygen, can be divided roughly into two large groups according to whether or not we can distinguish complex oxy-ions in the crystal. In the former case the compounds are described as oxy-salts, and in the latter as complex oxides. The complex oxy-ions in oxy-salts may be finite, *e.g.*, $SO_4{}^{2-}$, $CO_3{}^{2-}$, etc., or infinite in one, two, or three dimensions. Examples of the latter types found in silicates are the linear ions $(SiO_3)_n{}^{2n-}$ and $(Si_4O_{11})_n{}^{6n-}$ in pyroxenes and amphiboles respectively, the infinite layer ions in micas and chlorites, and finally the charged 3-dimensional framework ions in zeolites, which result from replacement by Al of part of the Si in a SiO_2 framework. For example, the framework in analcite has the composition $(AlSi_2O_6)_n{}^{n-}$, and the positive ions necessary for electrical neutrality are accommodated in the interstices of the framework. We shall be concerned here only with the complex oxides formed by the more metallic elements.

Crystals of these compounds consist of assemblies of oxygen ions with positive ions of various kinds. The number of oxygen ions surrounding a particular kind of metal ion is determined by the relative sizes of the ions : the larger the ion the greater its " co-ordination number ". As mentioned earlier, relatively few ions are comparable in size with the O^{2-} ion, so that the crystal structures of many ionic oxides (both simple and complex) are determined by the closest possible packing of the large oxygen ions. For this reason many oxide structures are closely related in the sense that the geometrical arrangement of the oxygen ions is the same and only the positions of some or all of the metal ions are different. The oxides FeO, γ-Fe_2O_3, and Fe_3O_4 are related in this way. This feature of oxide structures has a number of important consequences. First, it leads to the possibility of variable composition, a deficiency of metal ions being compensated by change of valency. Second, it is only the sizes of the positive ions which determine whether they may occupy certain positions between the close-packed oxygen ions. Isomorphous replacement is therefore common, some ions of one kind being replaced randomly by ions of another kind. If, however, the ions of different metals are arranged *regularly*, the phase is described as a complex oxide, and it has an ideal empirical formula which is usually simple. A third point is that there is also close-packing of O^{2-} and OH^- or of OH^- in some oxy-hydroxides and hydroxides respectively, in which case these compounds are closely related structurally to the oxides into which they may be converted. For example, in α-FeO·OH and α-Fe_2O_3 not only the oxygen atoms but also a proportion of the iron atoms are in the same positions in both structures. A crystal of α-FeO·OH can therefore be converted into what is essentially a single crystal of α-Fe_2O_3, but there is also the possibility that phases intermediate between the two extremes may result from incomplete conversion. Judging by published analytical figures, it appears to be difficult to prepare certain " oxides " free from water if they are made by heating hydroxides or oxy-hydroxides. This is the case with certain oxides of Fe, Co, and Mn. Thus α-Fe_2O_3 made by wet methods retains some water after calcining at quite high temperatures, and recent work on MnO_2 shows that it is not possible to obtain the anhydrous oxide by such methods. In addition to hydroxides, both iron and manganese form an oxy-hydroxide MO·OH, oxides MO, M_2O_3, and M_3O_4, and manganese also the dioxide MnO_2. Recent analytical results [16] for the best preparations of MnO_2 were expressed in percentages of MnO_2 (95·10), Mn_2O_3 (1·09), and H_2O (3·81), and analyses of materials described as " polymorphic forms " of MnO_2 have shown MnO_2 contents of the order of 90—93%.[17, 18, 19] It seems possible that in some of these cases the complications are due to phases intermediate between, say, $Mn^{III}O\cdot OH$, $Mn_2{}^{III}O_3$, and $Mn^{IV}O_2$. These facts enable us to appreciate why many oxide systems are so complex and also why it is impossible to understand their complexity except in terms of 3-dimensional arrangements of atoms.

Some Types of Complex Oxide Structure.—We may recognise two broad classes of structure :

(*a*) Complex oxide structures derived from the structures of simple oxides A_aO_n by

(i) *regular* replacement of A by B and C ; *e.g.*, $AlAsO_4$ with the same

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[16] J. T. Grey, *J. Amer. Chem. Soc.*, 1946, **68,** 605.
[17] P. Dubois, *Ann. Chim.*, 1936, **5,** 411.
[18] O. Glemser, *Ber.*, 1939, **72,** 1879.
[19] E. V. Alekseyevskii and K. V. Fried, *J. Gen. Chem. Russia*, 1945, **15,** 3.

structure as quartz (SiO_2), $FeTiO_3$ isomorphous with α-Fe_2O_3, $FeSb_2O_6$ with the trirutile structure (see later),

(ii) *random* replacement of A by B and C; *e.g.*, Li_2TiO_3 and $LiFeO_2$ with random rock-salt structures, $FeSbO_4$ with a random rutile structure,

(iii) joining together blocks of the A_aO_n structure by means of a small number of ions of a new type. Structures related in this way include: β-alumina, $NaAl_{11}O_{17}$, and γ-Al_2O_3, magneto-plumbite, $PbFe_{12}O_{19}$, and Fe_3O_4.

(*b*) New structure types, *e.g.*, perovskite structure for compounds ABO_3.

Of the numerous complex oxide structures we shall consider here only a few of the more important, and we shall be concerned with general structural principles rather than detailed descriptions of crystal structures.

The spinel structure, β-alumina, and related compounds. This is an important structure based on cubic close packing of oxygen atoms. The unit cell contains 32 oxygen atoms, and in the interstices there is room for 8 atoms surrounded tetrahedrally by 4 oxygen atoms and for 16 atoms surrounded octahedrally by 6 oxygen atoms. Many oxides AB_2O_4 have this structure—in particular the spinels, MAl_2O_4 (M is Fe, Co, Ni, Mn, or Zn)—but it is also adopted by certain oxides M_2O_3 and M_3O_4. Magnetite, Fe_3O_4, is one example, one-third of the ions being Fe^{2+} and the remainder Fe^{3+}, *i.e.*, $Fe^{II}Fe_2^{III}O_4$. The γ-form of Fe_2O_3 (and possibly also γ-Al_2O_3) [20] has a spinel-like structure deficient in metal ions, there being on the average only $21\frac{1}{3}$ Fe^{3+} ions per unit cell distributed at random among the eight tetrahedral and sixteen octahedral positions. Owing to this similarity in structure γ-Fe_2O_3 and Fe_3O_4 are easily interconvertible. In all the oxides FeO, Fe_3O_4, and γ-Fe_2O_3 the arrangement of oxygen atoms is the same (cubic close-packing). A cube with edge about 8·6 A. containing 32 O^{2-} ions can accommodate 32 Fe^{2+} ions in positions of octahedral co-ordination. This is the ideal structure of stoicheiometric FeO. Removal of some of these ions and replacement by two-thirds of their number of Fe^{3+} ions gives FeO deficient in iron, sometimes (incorrectly) described as FeO containing excess oxygen. If the process is continued until the same volume contains 24 iron atoms, we have Fe_3O_4. Further removal of iron gives γ-Fe_2O_3 with an average of $21\frac{1}{3}$ iron atoms for every 32 oxygen atoms.

The metastable γ-Al_2O_3 is not found in Nature but may be prepared by the dehydration of any hydrated aluminium oxides (except the oxyhydroxide diaspore which dehydrates directly to α-Al_2O_3) or of ammonium alum (at 1000°). It has a very small particle size and great absorptive power ("activated alumina") and is also used in the manufacture of synthetic sapphire in the Verneuil furnace. Another compound was once thought to be a third polymorphic form of Al_2O_3 and was named β-alumina. *X*-Ray investigation showed, [21], [22] however, that it has the composition $NaAl_{11}O_{17}$ ($Na_2O,11Al_2O_3$) and a definite structure closely related to that of spinel, no less than 100 of the 116 atoms in the unit cell being arranged in exactly the same way as in the spinel structure. The Na^+ ions are

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[20] See, however, M. H. Jellinek and I. Fankuchen, *Ind. Eng. Chem.*, 1945, **37**, 158.

[21] C. A. Beevers and S. Brohult, *Z. Krist.*, 1936, **95**, 472.

[22] C. A. Beevers and M. A. S. Ross, *ibid.*, 1937, **97**, 59.

situated between large blocks of the spinel structure and their presence is essential to the stability of the structure (Fig. 7). The structure of magnetoplumbite, $PbFe_{12}O_{19}$, is similarly built up of large portions of the magnetite (spinel) structure held together by Pb^{2+} ions. These structures are of interest, not only because they show how such extraordinary formulæ as $NaAl_{11}O_{17}$ and $PbFe_{12}O_{19}$ arise, but also because they emphasise the importance of relatively small numbers of comparatively large ions in stabilising complex structures of compounds which may be mistaken for simple metallic oxides.

The perovskite structure. As we have said already, the oxygen atoms in many oxide structures are close packed with the smaller positive ions in the interstices. For very large positive ions there is the alternative possibility that they and the oxygen ions together form a close-packed arrangement, smaller ions of other elements still occupying the spaces between four or six oxygen ions. This is the case in the perovskite structure, adopted by many compounds ABO_3, in which the large A ions are in contact with 12, and the smaller B ions with 6, oxygen ions. Recent work [23, 24] has shown that this structure is often slightly distorted from the ideal cubic form, but here we are concerned only with the general nature of the structure. Examples of compounds with the ideal perovskite structure include $SrTiO_3$, $BaTiO_3$, $LaFeO_3$, etc., the large Sr^{2+}, Ba^{2+}, and La^{3+} ions occupying positions of 12-co-ordination, and the small Ti^{4+} and Fe^{3+} ions positions of 6-co-ordination. The structure is closely related to that of

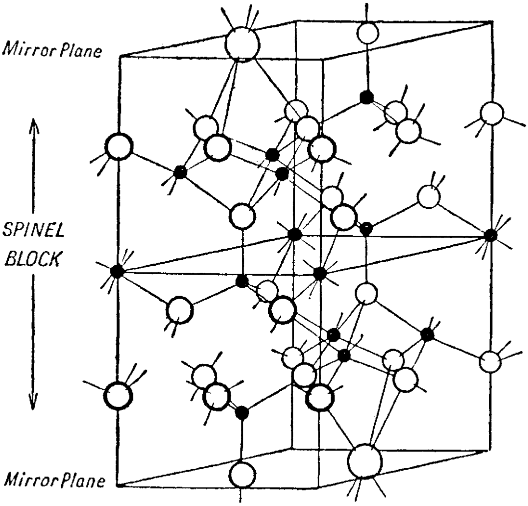

FIG. 7

The relation of the structure of β-alumina, $NaAl_{11}O_{17}$, *to that of spinel (after Beevers and Ross). Large circles represent* Na, *small ones* O, *and black circles* Al.

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[23] S. Naray-Szabo, *Naturwiss.*, 1943, **31**, 203, 466.

[24] H. D. Megaw, *Proc. Physical Soc.*, 1946, **58**, 133.

ReO_3 (see Fig. 8), and this is interesting in connection with the structure of the tungsten bronzes. The structure of WO_3 is apparently a slightly deformed version of that of ReO_3. Since tungsten can form both W^{5+} and W^{6+} ions we might expect to find that $NaWO_3$ has the perovskite structure. The tungsten bronzes are intermediate in composition between $NaWO_3$ and WO_3, and in fact the phases from $Na_{0\cdot32}WO_3$ to $Na_{0\cdot93}WO_3$ have the perovskite structure. There is random arrangement of the Na^+ ions, and for every Na^+ ion there must be one W^{5+} ion, so that we may formulate the tungsten bronzes $Na_xW_x^{5+}W_{1-x}^{6+}O_3$.

Recent studies of other oxide systems containing a metal which can exhibit more than one valency suggest that there may be much to learn about such metal-oxygen systems. For example, a number of phases intermediate between MoO_3 and MoO_2 have been identified by their *X*-ray photographs,[25] including blue-violet $MoO_{2\cdot9}$ (approximate composition) and reddish-violet $MoO_{2\cdot75}$ (*i.e.*, approximately Mo_4O_{11}). Vanadium also forms highly coloured semi-conducting compounds which contain V^{4+} and V^{5+} ions, with compositions approximating to the formulæ $Na_2O,V_2O_4,5V_2O_5$ and $Na_2O,V_2O_4,11V_2O_5$.[26]

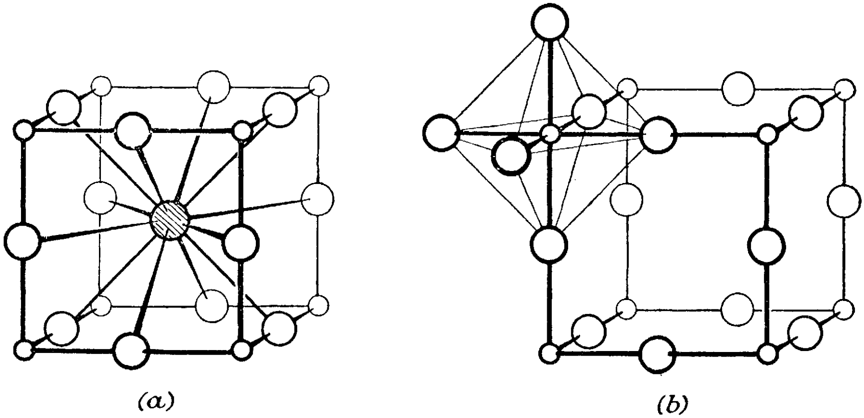
(*a*) (*b*)

FIG. 8

(*a*) *The perovskite structure for compounds* ABO_3. *Large open circles represent* O *ions, the shaded circle* A, *and the small circles* B *ions.* (*b*) *The crystal structure of* ReO_3.

Having shown that some oxide systems are far more complex than is suggested by the simple formulæ of the oxides, we shall conclude by indicating how the study of crystal structures enables us to systematise the oxygen chemistry of a particular element (antimony) by demonstrating the essential simplicity of the underlying structural principles.

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[25] G. Hägg and A. Magnéli, *Arkiv Kemi, Min. Geol.*, 1944, **19***A*, No. 2.

[26] H. Flood and H. Sørum, *Tids. Kjemi Berg.*, 1943, p. 55; 1946, pp. 32, 59.

The Oxygen Chemistry of Antimony

Comparatively little is known of the structures of oxy-compounds of tervalent antimony other than the two forms of the trioxide and certain complex oxides such as $ZnSb_2O_4$. In all these compounds Sb^{III} (like P^{III} and As^{III}) forms three pyramidal bonds. The compound $ZnSb_2O_4$ is of interest since it has the same structure [27] as Pb_3O_4 (Fig. 4), Sb^{III} replacing Pb^{II}, and Zn^{II} replacing Pb^{IV}. The maximum observed oxygen co-ordination numbers of the elements of Group V in the quinquevalent state in crystalline oxy-salts are :

		V	Nb	Ta	(A sub-group)
N	P				
		As	Sb	Bi	(B sub-group)
3	4	4 and 6	6		

(Vanadates and arsenates containing complex oxy-ions are based, like phosphates, on tetrahedral MO_4 co-ordination groups, but 6-co-ordinated As apparently occurs in $CaAs_2O_6$ and related compounds, and 6-co-ordinated V^V in $BiVO_4$ and $RhVO_4$, to which a statistical rutile structure has been assigned.)

The oxygen chemistry of quinquevalent antimony was formerly very perplexing, and many compounds—some anhydrous, some hydrated—have been described as ortho-, meta-, and pyro-antimonates and assigned formulæ analogous to those of phosphates. As the result of the study of the structures of many of these compounds, which exist only in the crystalline state, it is now known that their structural chemistry is very simple and quite different from that of phosphates, arsenates, and vanadates, being based not on tetrahedral but on octahedral co-ordination of Sb^V by oxygen. Many of the old formulæ require revision. The compounds in question fall into two main groups :

(*a*) Salts containing $[Sb(OH)_6]^-$ ions (hexahydroxyantimonates).

(*b*) Mixed oxides of the following (and possibly other) types, based on octahedral SbO_6 co-ordination groups: M^ISbO_3, $M^{II}Sb_2O_6$, $M^{III}SbO_4$, $M_2{}^{II}Sb_2O_7$.

One great simplification is due to the fact that antimony does not form finite oxy-ions such as $SbO_4{}^{3-}$ and $Sb_2O_7{}^{4-}$ analogous to those of phosphorus. Compounds formerly described as antimonates fall into one or other of the above two classes, and contain octahedrally co-ordinated antimony, either as $Sb(OH)_6{}^-$ ions in compounds which were called hydrated meta- or pyro-antimonates, or as 6-co-ordinated Sb^V in the complex oxides of class (*b*).

(*a*) *Salts containing* $Sb(OH)_6{}^-$ *Ions.*—We are not particularly concerned in this article with these hexahydroxyantimonates, and we shall simply

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[27] S. Ståhl, *Arkiv Kemi, Min. Geol.*, 1943, **17***B*, No. 5.

note a few cases where structural studies have indicated the correct structural formulæ :

Old formula.	Correct structural formula.
$LiSbO_3,3H_2O$	$Li[Sb(OH)_6]$
$Na_2H_2Sb_2O_7,5H_2O$	$Na[Sb(OH)_6]$
$Mg(SbO_3)_2,12H_2O$	$[Mg(H_2O)_6][Sb(OH)_6]$
$Cu(NH_3)_3(SbO_3)_2,9H_2O$	$[Cu(NH_3)_3(H_2O)_3][Sb(OH)_6]_2$

The removal of sodium " pyroantimonate " from the text-books should now be only a matter of time. The partial hydrolysis of $NaSbF_6$ yields a salt originally formulated as $NaF,SbOF_3,H_2O$. Its correct formulation as $Na[SbF_4(OH)_2]$ brings it into line with the hexahydroxyantimonates.

(*b*) *Mixed Oxides based on* SbO_6 *Co-ordination Groups.*—In some cases the structures are similar to those of simple ionic oxides, *e.g.*, $NaSbO_3$ with the same structure as ilmenite ($FeTiO_3$) and hæmatite (α-Fe_2O_3), $FeSbO_4$ with a statistical rutile structure, and $ZnSb_2O_6$ with the trirutile structure. There is therefore no reason for describing these compounds as " antimonates ".

M^ISbO_3. The compound $NaSbO_3$ is dimorphic, one form being isomorphous with $FeTiO_3$ and the other being closely related to a number of complex oxy-compounds of antimony, bismuth, niobium, and tantalum.[28, 29, 30] All the following compounds have very similar structures: $CaNaNb_2O_6F$, $CaNaSb_2O_6(OH)$, $BiTa_2O_6F$, $Sb_3O_6(OH)$, $NaSbO_3$, and $AgSbO_3$. The fourth of these is of interest in connection with the " tetroxide ", Sb_2O_4. When hydrated Sb_2O_5 is heated (at about 800°) it is not converted directly into Sb_2O_4, as was at one time supposed, but into $Sb_3O_6(OH)$, and the latter is converted into Sb_2O_4 only by prolonged heating at 900°. This oxide is isomorphous with $SbTaO_4$,[31] and may therefore be written $Sb^{III}Sb^{V}O_4$.

$M^{II}Sb_2O_6$. Three types of structure have so far been found for these compounds, which were formerly described as " meta-antimonates " $M(SbO_3)_2$ of bivalent metals. The first group of compounds, MSb_2O_6 and MTa_2O_6 (where M = Mg, Fe, Co, Ni), have the trirutile structure [32] (Fig. 9), the unit cell of which corresponds to three unit cells of the simple rutile structure with the Ti^{IV} replaced in a regular way by M^{II} and Sb^{V}. This structure is possible for these compounds because the radii of the positive ions are all very similar (0·60—0·75 A.). For larger ions M^{2+} this structure is not possible and a hexagonal structure is adopted if the radius of M^{2+} is about 1 A. or more.[33] In this structure, illustrated in Fig. 10, the M and Sb atoms are segregated in layers, and ions ranging from Ca^{2+} (0·99 A.) to Ba (1·35 A.) can be accommodated by pushing the Sb–O layers further apart. Thus although the *a* dimension of the unit cell remains remarkably

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[28] N. Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241.

[29] O. Zedlitz, *Z. Krist.*, 1932, **81**, 253.

[30] O. Rosén and A. Westgren, *Geol. För. Förh.*, Stockholm, 1938, **60**, 226.

[31] K. Dihlström, *Z. anorg. Chem.*, 1938, **239**, 57.

[32] A. Byström, B. Hök, and B. Mason, *Arkiv Kemi, Min. Geol.*, 1941, **15***B*, No. 4.

[33] A. Magnéli, *ibid.*, No. 3.

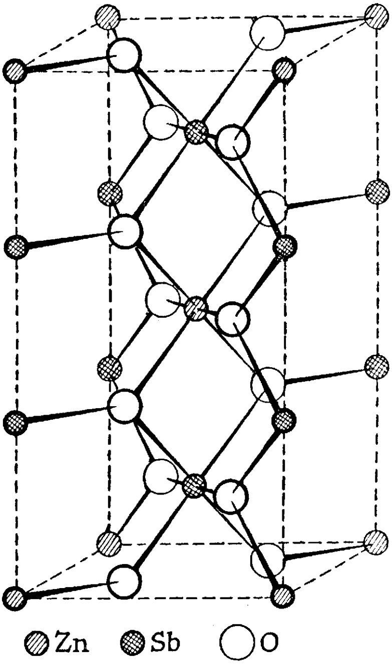

FIG. 9
The crystal structure of $ZnSb_2O_6$ (*trirutile structure*).

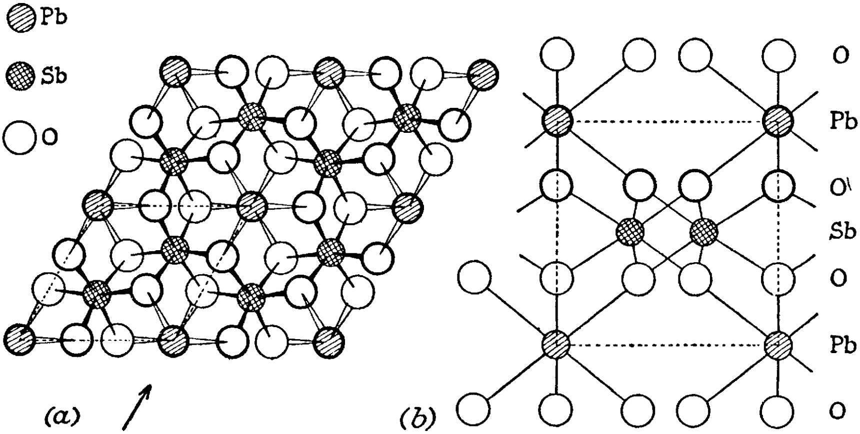

FIG. 10
The crystal structure of PbS_2O_6 : (*a*) *plan*, (*b*) *elevation* (*viewed in the direction of the arrow*), *on a slightly larger scale.*

constant, the c dimension (perpendicular to the plane of the layers) shows a very large increase from the calcium to the barium compound:

	Ionic radius, A.	a, A.	c, A.
Ca . . .	0·99	5·222	5·010
Sr . . .	1·13	5·251	5·332
Ba . . .	1·35	5·289	5·741

A third structure, adopted by $MnSb_2O_6$, $MgNb_2O_6$, $ZnTa_2O_6$, etc., is related to the trirutile structure in much the same way as the structures of brookite and rutile (two of the three polymorphic forms of TiO_2) are related; it does not merit description in this brief survey.

$M^{III}SbO_4$.—A number of complex oxides of this type have been shown [34] to crystallise with a statistical rutile structure, *i.e.*, the M^{III} and Sb^V atoms occupy at random the Ti^{IV} positions in that structure. Examples include $FeSbO_4$ and $AlSbO_4$.

[34] K. Brandt, *Arkiv Kemi, Min. Geol.*, 1943, **17***A*, No. 15.