

Anion Coordination and Cation Packing in Oxides*

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It is shown by considering a few examples that oxide structures are usefully described in terms of their cation packings and the coordination of the anions by these cations. This, together with a consideration of nonbonded repulsions between the atoms, leads simply to a rationalization of some crystal structures and coordination numbers, and to an understanding of the volume changes in certain phase transitions.

Introduction

The traditional description of "ionic" crystals focuses almost exclusively on the coordination of the cation by anions and on the geometry of the anion packing. In the case of compounds of the lighter electro-negative elements (i.e., nitrides, oxides, and fluorides) it is our thesis that this leads to, at best, an incomplete understanding of their crystal chemistry. In this article, as indicated by its title, we attempt to show how the complementary viewpoint leads to many new insights. We wish to heed the admonition of Wells (*1*) to consider the purely geometrical constraints on crystal structure. These constraints require one to consider both anion coordination and cation coordination as equally important in deter-

mining crystal structure. In Wells' words, "Emphasis on the coordination group of the cation has led to a tendency to underestimate the importance of coordination of the anion" (*1*).

Geometrical constraints are conveniently divided into topological and metric aspects (although it is not always possible to separate them). Wells (*1*) has examined certain aspects of these, and we cannot do better than to quote him again: ". . . geometrical and topological factors . . . have a direct bearing not only on the details of molecular and crystal structures but also on the stability and indeed existence of some compounds. In spite of their relevance to structural problems, some of the factors . . . seem to have been completely ignored."

Our intention here is to attempt to reduce this area of ignorance and also to add a factor (the consideration of the *nonbonded* sizes of atoms) that we feel is more useful in discussions of coordination numbers than

* Dedicated to Professor A. F. Wells on his 70th birthday.

the ionic model (in which ionic radii are the only determinant).

Geometrical Constraints on Crystal Structures

A familiar example of a topological constraint is the famous Euler condition applied to tessellations of the Euclidean plane (or a torus),

$$P - E + V = 0, \quad (1)$$

in which P is the number of polygons, E the number of edges, and V the number of vertices. This, and equations derived from it, provide an essential basis for a discussion of, among other things, plane nets (1, 2). On the infinitely more difficult problem of three-dimensional nets there is very little other than Wells' pioneering work available (3). Two aspects of topological constraints deserve attention. The first is that they give rise to diophantine equations (ones in which only solutions in positive integers are admitted) such as Eq. (1). The second is that they often provide necessary, but not sufficient, conditions for the existence of a structure, a fact that contributes to making the subject at once so difficult and so fascinating. A simple example (2) might illustrate the latter point. A plane net (or tessellation) with Schläfli symbol $5^2 \cdot 10$ satisfies Eq. (1), but in this case other simple topological arguments demonstrate that it cannot exist. These arguments do not however readily lend themselves to generalization to cover more complicated nets.

Another example of a topological constraint is provided by the celebrated electrostatic valence sum rule of Pauling. The Pauling bond strength of a cation of charge Z_i and coordination number N_i is $s = Z_i/N_i$. Pauling's rule then states that for the cations bonded to each anion of charge Z_x

$$\sum(Z_i/N_i) = Z_x. \quad (2)$$

In practice of course, Nature is some-

what tolerant and permits small deviations from Eq. (2), in which instance generalizations of the concept of bond strengths prove useful, but, as written, Eq. (2) is another example of a diophantine equation.

A third topological constraint is one that is so obvious as to be almost trivial, yet it has some profound consequences. Consider a crystal $A(1)_{n_1}A(2)_{n_2} \dots X(1)_{m_1}X(2)_{m_2} \dots$, in which the cations $A(i)$ have coordination numbers $N_{A(i)}$ and the anions $X(i)$ have coordination numbers $N_{X(i)}$. Then

$$\sum n_i N_{A(i)} = \sum m_i N_{X(i)}. \quad (3)$$

The topological origin of this equation is simply that each bond has a cation at one end and an anion at the other. Clearly then it is not applicable to polycompounds.

We note in passing that the electrical neutrality condition

$$\sum n_i Z_{A(i)} = \sum m_i Z_{X(i)} \quad (4)$$

is not independent of, but follows directly from, Eqs. (2) and (3).

Metric constraints refer to distances and angles. Even simple examples have far-reaching consequences. One is that for 3-coordinated AX_3 the $X-A-X$ bond angles cannot exceed 120° (see below). Wells (1) cites the example of 4-connected nets in which rings of four atoms occur (such as in the β -BeO structure). It is impossible in such a structure for more than half the atoms to have regular tetrahedral coordination, as at most two of the angles of each ring of four bonds can be $109^\circ 28'$.

A constraint with far-reaching consequences and that leads quickly to difficult and unsolved problems is the requirement that cation \dots cation and anion \dots anion distances exceed bonded cation-anion distances. There is no a priori reason for this to be true, and indeed it is not in substances such as peroxides with O-O bonds, but in the absence of metal-metal or anion-anion bonding it is a very good working hypothesis. This constraint provides an upper limit

of 12 to coordination numbers. An example is provided by the structure of WAl_{12} . In practice the maximum coordination numbers for different compositions are less. For compounds AX , the limit appears to be 8 and we know of no example of an oxide in which the average cation (or oxygen) coordination number exceeds 9. If the last number is accepted as an upper limit then it follows at once that for an oxide M_2O (e.g., Rb_2O) at least half the cations must have a coordination number ≤ 4 , despite anything "radius-ratio rules" might have to say to the contrary. Closely related is the observation (1) that no more than two coordination octahedra or four coordination tetrahedra can share only a common vertex. As we show below this has interesting consequences.

One further point deserves mention under this heading. Nature has been far more generous in providing us with cations than with anions and, until recently anyway, we have further biased the situation by studying almost exclusively crystals with several cations but only one anion. In such instances cation-centered coordination polyhedra are often fairly regular but anion-centered coordination polyhedra quite irregular. As a consequence anion arrays are sometimes related to simple packings but in ternary, etc., oxides the cation arrays are those of more complex packings often such as occur in alloy structures.

Anion Coordination and "Close Packing"

In the description of atomic arrays we prefer *not* to use the term "close-packing" which conjures up a mental image of spheres in contact, but use instead the term *eutaxy* (4) for arrays which are (approximately) the same arrangement as the centers of closest-packed spheres. When arrangements of connected tetrahedra and octahedra are considered we also use the term topological eutaxy. The reason for this

is that eutactic arrays can arise purely from the geometrical constraints on crystal structure. The fact that oxygen arrays are often eutactic in certain classes of oxide crystals has led to the idea (in our opinion, completely mistaken) that the crystal is composed of large anions "in contact" with small cations in the interstices.

A little reflection would show that the very frequent occurrence of anti-structures (fluorite and anti-fluorite are familiar examples) indicates that the occurrence of a particular atomic arrangement cannot lead directly to any inference about relative atomic sizes. Therefore it is worth inquiring why oxides have eutactic anion arrays so frequently (though not nearly as frequently as the text books would have one believe!). To do this we start with cation-centered coordination polyhedra that are octahedra and/or tetrahedra and connect them to make a crystal structure.

If the structure has only corner-connected octahedra, and as only two octahedra can share a common vertex, the composition is MO_3 . The simplest possible arrangement is the familiar cubic ReO_3 structure. This can be described as "cubic-closest packed with one-quarter of the atoms removed" but we note that in the *topological* sense there is hexagonal eutaxy. This is because (5) the structure can be deformed without breaking any bonds, or destroying the regularity of the octahedra, into metrically perfect hexagonal eutaxy.

Other MO_3 structures are of course possible: the common pyrochlore framework (such as occurs for example in $(Ag)SbO_3$) is not eutactic and is also rigid, in the sense that it cannot be deformed without deforming the octahedra.

When one considers corner-connected tetrahedral arrays with composition MO_2 , the very many aluminosilicate frameworks (such as in feldspar) come to mind. With reasonably regular tetrahedra, the anion arrays are very far from eutactic and, with

one interesting exception, are not eutactic in the topological sense. The exception is the cristobalite framework which is topologically equivalent to *both* hexagonal and cubic eutaxy (6). In its least dense arrangement the anion array is that of "cubic close packing with one-half the atoms removed." It can be deformed without breaking bonds or deforming the tetrahedra into hexagonal eutaxy, such as occurs in orthorhombic ZnCl_2 (7), or into cubic eutaxy as in $(\text{Cu})\text{FeS}_2$ or (approximately) in $\alpha\text{-ZnCl}_2$ (8). A very large number of intermediate structures are known (6).

In contrast to the noneutactic arrays usually found when the anion/cation stoichiometric ratio is large (as in the examples cited above), when the anion/cation ratio is lower one finds that with octahedral and/or tetrahedral coordination of the cations, topologically eutactic arrays almost always occur in binary crystals. The reason for this is found by examining the coordination of the anions by the cations. This must be as regular as possible to maximize $M \cdots M$ distances (i.e., the cation arrangement must be isonomous (9)).

We consider just one example, that of octahedral coordination and composition MO_2 . Octahedron edge sharing is necessary so that with regular octahedra, a $M\text{-O-M}$ bond angle of 90° and a short $M \cdots M$ distance occur. With anion coordination OM_3 a third octahedron must be connected to each oxygen, and with $M \cdots M$ distances made as large as possible one immediately arrives at the configuration shown in Fig. 1. As can be seen from the figure this is already (approximately) an element of hexagonal anion packing. Units as drawn in Fig. 1 can only be put together in one way; the rutile structure is the result. In the real rutile structure of course the polyhedra distort to make OM_3 more nearly an equilateral triangle. With the unit of Fig. 1 distorted to exactly an element of hexagonal packing, they can be joined together so that

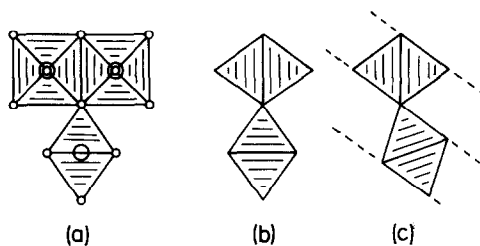


FIG. 1. (a) A third regular octahedron sharing a corner with two octahedra sharing a common edge in such a way as to maximize the distance between the atoms at the center of the octahedra. (b) The same viewed at an angle of 90° from that in (a). (c) Showing how an element of hexagonal eutaxy ("close-packed" layers indicated by dashed lines) is obtained from the figure in (b).

instead of opposite edges, other pairs of nonadjacent edges of a given octahedron are shared. The $\alpha\text{-PbO}_2$ structure results. With regular octahedra the anion arrangement is not constrained to be exactly in hexagonal eutaxy, and the anion coordination is less isonomous.

With OM_3 coordination and MO_4 tetrahedra, the very open phenacite or $\beta\text{-Si}_3\text{N}_4$ structure results (with almost equilateral OM_3). This structure is also topologically eutactic in the same way as the cristobalite structure is.

Similar arguments applied to composition M_2O_3 and MO_3 octahedra lead directly to the corundum structure as the most favorable (the one with most isonomous OM_4 tetrahedra). With "large" cations, Nature prefers to have a regular OM_4 tetrahedron, but very irregular MO_6 figures as in the bixbyite structure.

The Nonbonded "Sizes" of Atoms

It is clear that the bonding in crystals such as silicates is very similar to that in small molecules such as, for example, disilyl ether, $(\text{SiH}_3)_2\text{O}$. As emphasized particularly by Gibbs and his co-workers (10), structural details such as Si-O bond lengths and Si-O-Si bond angles are essentially

the same in both molecules and crystals. Less well known, but equally true, is the fact that bond energies in such crystals and molecules are virtually identical. In fact even force constants are transferable from molecules to crystals (11). These facts suggest that a unified, covalent, description of bonding in both molecules and crystal should be adopted. From this point of view one is lead naturally to consider that atoms such as Si are larger than lighter atoms such as O.

It has long been recognized (12) that bond angles $A-X-B$ (where $X = C, N,$ or O) in molecules can be rationalized by a consideration of $A \cdots B$ nonbonded repulsions, and that indeed to a first (good) approximation $A \cdots B$ distances are given by a sum of *nonbonded radii* (R) assigned to A and B (12, 13). We (5) have applied these radii to crystal structures such as the cristobalite forms of SiO_2 , $AlPO_4$, etc., which consist of flexible frameworks of corner-connected tetrahedra. We showed that, together with the known expected bond lengths, these radii predicted very well the $A-O-B$ bond angles (which vary over a wide range) in these oxides.

Nonbonded radii, are of course, just a first approximation to a nonbonded potential $V(d)$, where d is the atom \cdots atom distance. We have reviewed elsewhere (14) what is known about $V(d)$ and its relationship to nonbonded radii R . It is sufficient to note here that (excluding hydrogen) the smallest atoms in this nonbonded sense are, in order of increasing size, F, O, and N, and that they are significantly smaller than atoms such as Al, Si, P, Si, etc. Thus in the hard-sphere approximation of nonbonded radii, $R(O) = 1.12 \text{ \AA}$, $R(Si) = 1.53 \text{ \AA}$.

Once it is conceded that cations may be, in this sense, larger than anions, one is let naturally to consider the role of cation \cdots cation repulsions in defining the coordination of anions by cations and in determining the cation packing in crystals. (For conven-

ience only, we continue to use the terms cation and anion for the more electropositive and the more electronegative elements, respectively.)

Coordination Numbers

Coordination numbers in crystals are determined by the delicate balance between bonded and nonbonded forces, and the constraints of stoichiometry. The "radius-ratio" criterion sometimes applied does not work as it employs inappropriate ionic radii rather than nonbonded radii. When the latter are used it is the coordination of the (smaller) anion by the (larger) cations that is usually significant. The hard-sphere model implied by radius-ratio rules is much too naive for quantitative predictions; nevertheless, it does provide useful insights.

Consider for example the coordination of oxygen by silicon. With normal bond lengths and threefold coordination silicon atoms would be forced to be much closer than twice the nonbonded radius so that normally (i.e., in low-pressure structures) oxygen is expected to be coordinated by no more than two silicon atoms. (Stated differently a preferred Si-O-Si bond angle of $\approx 145^\circ$ precludes 3 coordination.) Stoichiometry of SiO_2 then dictates a maximum coordination number of 4 for silicon. Note that octahedral coordination of Si in SiO_2 is precluded because Si is too "big" for OSi_3 , *not* because O is too "big" for SiO_6 ! Indeed if the constraint of stoichiometry is relaxed, SiO_6 coordination is observed in normal-pressure structures such as SiP_2O_7 (in which all oxygen atoms are 2-coordinated) and in structures with $Si(OH)_6$ groups (15).

Cation Packing

From the foregoing it should be clear that it would be useful to consider oxide structures in terms of cation packings. This is a very large undertaking, but one that we

have under way. We are helped immensely in this by the fact that in very many instances the cation packings are known alloy structures—with hindsight, this is not surprising. Some examples have long been known (e.g., spinel) but many do not appear to have been recognized. We discuss a few simple, but important, examples below.

Garnet

Garnets, typified by grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, have a structure that is very complex when considered in terms of cation-centered polyhedra. Three coordinates (x , y , z) are required to specify the anion positions, but the cations are all in special positions at the intersections of symmetry elements. The cation array is simply related to the Cr_3Si (A15) structure type with Al in the Si position and Ca and Si ordered on the Cr positions (16). Space is thus divided into irregular tetrahedra whose vertices are, however, fixed. Oxygen atoms center all the Ca_2AlSi tetrahedra. By requiring that the bond lengths be the normal ones for various bonds, it is easy to calculate the oxygen coordinates x , y , z and the unit cell parameter, a . (One tends to forget that in the early days of X-ray crystallography, light atom positions were often thus determined—and that this was the original and only intended use of atomic radii.) The description of the anion packing is much more difficult. It has been described as a packing of rods of alternating octahedra and trigonal prisms, but variations of anion parameters from one composition to another are difficult to understand on this basis (17).

Spinel and Olivine

It has long been recognized that the cation positions in a normal spinel (e.g., MgAl_2O_4) are those of the cubic Friauf-Laves phases (MgCu_2). Again space is divided into tetrahedra with vertices fixed by the symmetry. Oxygen atoms fill all the

MgAl_3 tetrahedra, and again the unit cell parameter and oxygen coordinates are immediately obtained from the expected Mg–O and Al–O bond lengths. Although the oxygen arrangement is topologically one of cubic eutaxy, in most spinels it is quite far from eutactic in the metric sense. The MgCu_2 structure has long been recognized as an efficient space filling with spheres of two different sizes, a consideration of some significance in discussions of pressure-induced phase transitions.

The structure of a typical olivine (18) is shown in Fig. 2. On the right are shown the SiO_4 tetrahedra and the Mg atoms, and on the left just the cation array. The latter is that of Ni_2In —a common structure type. It consists of Si-centered Mg_6 trigonal prisms connected in such a way that each prism has three caps. Note that in both olivine and Ni_2In there are three crystallographically different metal atoms. We just mention here that the cation packing description also provides a very elegant description of

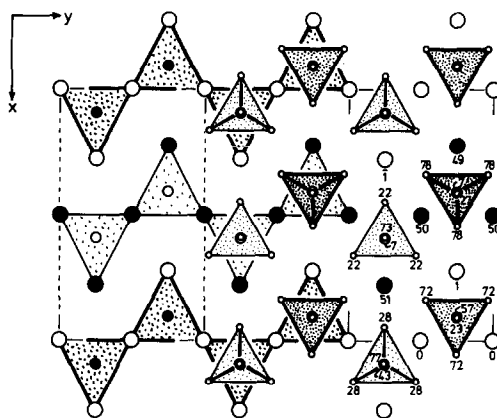


FIG. 2. The structure of olivine projected on (001) (setting $Pnma$). The right-hand part of the drawing shows SiO_4 tetrahedra and Mg atoms (large circles). Numbers are heights ($100z$). On the left the SiMg_6 trigonal prisms are shown. These are connected into columns parallel to the projection axis by sharing triangular faces, and the columns are joined into corrugated sheets by sharing prism edges. Alternate sheets are at heights differing by $z = \frac{1}{2}$.

the complex humite minerals $n\text{Mg}_2\text{SiO}_4$, $\text{Mg}(\text{OH},\text{F})_2$ (19, 20).

The Olivine-Spinel Phase Transition

One important indication of the relative sizes of atoms comes from examination of the effect of pressure on crystals that do not compress isotropically. In such experiments it would appear reasonable to suppose that of the short interatomic distances, those that decrease the least are those between atoms repelling each other the most. In olivine (Mg_2SiO_4) the results (21) are revealing. There are four sets of short $M \cdots M$ and $O \cdots O$ distances (corresponding to rings of four atoms $MOMO$). As we have discussed elsewhere (14), the changes with pressure strongly suggest that repulsive forces between $O \cdots O$ at approximately 2.6 Å are less than those between $\text{Mg} \cdots \text{Mg}$ at approximately 3.0 Å or $\text{Si} \cdots \text{Mg}$ at approximately 2.7 Å. An analysis of the olivine-spinel phase transition reinforces this conclusion.

This phase transition occurs with a large decrease in volume although there is no change in the primary coordination of the atoms. Until recently, this had not been very satisfactorily explained, but we have shown (22) that it becomes immediately understandable when the cation packing is considered. Thus the fairly open packing in olivine with SiMg_8 coordination transforms to the more efficient packing of the Friauf-Laves phase structure with coordination SiMg_{12} . This permits the $\text{Si} \cdots \text{Mg}$ distances to increase substantially (to 3.37 Å) in the denser phase, suggesting very strongly that it is the increasing $\text{Si} \cdots \text{Mg}$ repulsion energy that provides the driving force for the phase transition.

Zircon, Scheelite, and the Zircon-Scheelite Phase Transition

These two structures are considered because zircon (ZrSiO_4) transforms to the scheelite (CaWO_4) structure under pressure

(23) and, just as in the olivine-spinel transition there is a large (11%) decrease in volume but no change in primary coordination which is OZr_2Si (i.e., ZrO_8 and SiO_4).

The zircon structure is very simply related to that of rutile (TiO_2). The cation arrays are almost identical as illustrated in Fig. 3, with Zr and Si ordered on the Ti sites of TiO_2 (which are body-centered tetragonal as in $\beta\text{-Hg}$). Each Zr_2Si triangle is centered by oxygen.

The cation array of scheelite is a slightly distorted version of cubic eutaxy with, of course, ordered Ca and W. This is not a known alloy structure, but the same array also occurs in the pyrochlore structures of AgSbO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$. Just as zircon is simply related to rutile, scheelite is simply related to fluorite, the difference between the

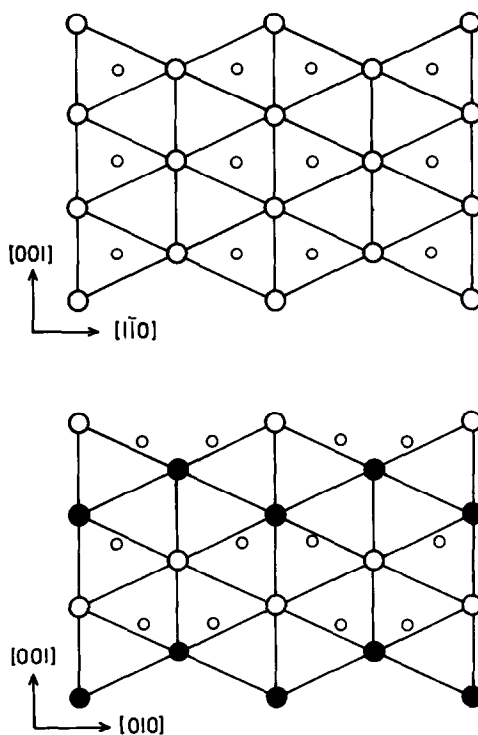


FIG. 3. Top: A (110) layer of TiO_2 (rutile). Large circles, Ti; small circles, O. Bottom: A (100) layer of ZrSiO_4 (zircon) to the same scale. Large open circles, Zr; large filled circles, Si; small circles, O.

last two structures simply being that oxygen moves from the center of the tetrahedral sites (Ca_2W_2 in scheelite) into Ca_2W triangles.

It is surely significant that the volume change in the zircon–scheelite phase transition is very similar to that in the well-known rutile–fluorite phase transition. Again an examination of metal · · · metal distances is revealing. In the low-pressure (zircon) form of ZrSiO_4 the shortest of these is $\text{Zr} \cdot \cdot \cdot \text{Si} = 2.991 \text{ \AA}$; in the high-pressure form the shortest such distance is $\text{Zr} \cdot \cdot \cdot \text{Si} = 3.347 \text{ \AA}$.

Conclusion

In this paper we have attempted to present the *rationale* of our approach to oxide structures. A central feature of it is the belief that cation · · · cation repulsions play a much larger role in determining structure than is usually admitted. We do not, of course, deny the existence of anion · · · anion repulsions or that in some instances they may be of importance. Rather, we realize that observed structures are a result of a balance between all forces, attractive and repulsive, between like and unlike atoms.

We have shown with a few examples that a deeper insight into oxide structures may be obtained by considering the cation packing (rather than the anion packing) and the anion coordination within these arrays. Many other examples could have been given; we plan to do this (19).

Acknowledgments

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