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The Structon Theory, Applied to Crystalline Silicates and Related Compounds[1]

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The structures of anions in which Si, P, B, and/or Al atoms are tetrahedrally surrounded by oxygen atoms are discussed. Using well-established principles one can deduce, from the over-all formula, the types and relative numbers of *structons* in these anions and also certain other structural characteristics. The structon types in pure silicates, for example, are: Si(4O''), Si(O', 3O''), Si(2O', 2O''), Si(3O', O''), Si(4O'), O'(Si), and O''(2Si), where O' and O'' designate nonbridging and bridging oxygen atoms, respectively.

Introduction

This paper deals with the principles underlying the structures of crystals, a subject with which the author has been concerned for nearly a half-century.[2-8] It deals particularly with the structures of silicates and related compounds and minerals, in which atoms of phosphorus, boron, and/or aluminum play a similar role to that of silicon in pure silicates. It is an amplification and extension of part of a recently published paper, dealing with macroanions in inorganic crystals and glasses.[9]

General Principles

Let us first consider briefly some important general principles of crystal structure. The most important principles are of course the same as those applying to stable arrangements of atoms in molecules, liquids, and glasses. For example, *the principles of interatomic bonding*, as introduced by Lewis[10] and extended by many others,[11-13] *are as applicable to crystals as to small molecules and ions.*[2,3] In many cases these principles determine the close-neighbor arrangements around each atom uniquely or at least greatly limit the possibilities, in molecules, ions, and crystals in which the atoms are held together by electron-pair bonds.

The influence of an atom on other atoms decreases very rapidly with distance (especially if no coulombic forces are involved); *hence for many purposes all interactions except those between closest neighbors can be neglected.*[7] This principle lies at the basis of the "structon theory."[14-16] In this theory attention is focused on the close-neighbor arrangements of the atoms and on the relationships between numbers and types of close-neighbor structures (structons), the complete structure,

and the magnitudes of various "structon-additive" properties. This paper deals in some detail with certain applications of the structon theory.

Atoms of a given kind, crystallizing in the same environment, *tend to be surrounded* (by close neighbors) *similarly*, giving structons of the same type. They may not be similarly surrounded, however, if, as in many organic compounds, the local environments were determined, before crystallization, by forces stronger than those effective during the crystallization[7] or if two or more local arrangements have practically the same energy. These limitations are of importance in determining whether a given composition solidified as a glass or a crystal.

The tendency for like atoms to have like environments results, in part, from the facts (1) that there is usually one type of local environment that is significantly more stable than any other and (2) that changes from one type of local structure to another can take place readily under the conditions existing when the structure is becoming fixed. This tendency is inapplicable with respect to the arrangements of oxygens around the cations in many silicates, in which different conformations of the silicate anions and different distributions of oxygens around the cations have nearly the same energy.

Another general and important principle is that, other factors being equal, *the most stable structure is that having the lowest coulombic energy.* The requirement that the structure as a whole must be electrically neutral, neglecting surface charges, can be considered a corollary of this principle. Another corollary is that, other things being equal, the most stable structure is that giving neutrality in as small a volume as possible. The tendency for positively charged ions to have as close neighbors only negatively charged ions can be considered an example of this local neutrality principle, as can the charge balancing inherent in Pauling's "electrostatic valence rule."[13]

The term "crystal structure" includes, in addition to the pattern of the arrangement of the atoms, the distances between them. The distance between the centers of two adjacent atoms depends on a complex summation of forces or energies, including both those for direct interaction between these two atoms and those for other more distant pairs of atoms. Nevertheless, for reasons that are qualitatively readily explainable but which need not be discussed here, it is possible to

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deduce sets of *atomic radii*,[17-21] ionic radii,[13,22-25] and van der Waals radii[8,13,26] that, *by appropriate addition, give interatomic distances* in approximate agreement with those obtained more directly from experiment.

If an atom is held to its neighbors primarily by electron-pair bonding forces, the coordination number is determined chiefly by the numbers of bonding electrons, the numbers and orientations of the orbitals available to them, and the bond energies associated with occupancy of these orbitals. If, however, the attractions between an atom and its neighbors are largely coulombic, it tends to surround itself by as many neighbors of opposite charge as is possible, without forcing these neighbors so close together that their mutual repulsion energy becomes large. In terms of the constant ionic radius approximation, the maximum coordination number of an ion of a given element, for neighbor ions of another given type, depends on the ratio of the ionic radii.[22,27,28] Similar ideas apply to complex crystal structures, such as those of the silicates, in which the atoms immediately surrounding a cation, although not monatomic anions, are (oxygen) atoms holding excess negative charges. Each is bonded to a silicon or other atom by bonds which possess some polarity. In these cases, also, geometrical limitations imposed by the structures of the complex anions also greatly affect the coordination numbers of the cations.

The author takes the point of view that it is convenient and justifiable to consider each internally bonded ensemble of atoms (Si, B, P, and/or Al, with the oxygens tetrahedrally bonded to them, in the crystals considered in this paper) as an anion, realizing, however, that the bonds in such an anion are, in fact, partially polar and that the attractions between the cations and their oxygen neighbors often "possess some covalent character." The author believes that this point of view is better, for many purposes, than the approximation, often adopted, that each oxygen is an anion and each Si, B, P, and Al is a cation.

One justification for this point of view is that otherwise one would expect the preferred bond angle in oxygen bridges to be 180°, whereas actually these bridges are bent, with only a very few possible exceptions (*e.g.*, $Sc_2Si_2O_7$,[29] $CaAl_2Si_2O_8$).[30] In several other crystals oxygen bridges have been reported to be collinear, but later, more precise work has shown them to be, in fact, bent. It seems likely that the individual bridges are bent also in the remaining apparent exceptions, the bending being undetected because of the time and space averaging inherent in the X-ray diffraction method.[31,32]

The van der Waals forces between all pairs of atoms, at distances larger than the equilibrium distance, are attractions. To minimize the energy, therefore, *the structure tends to be as close-packed as possible*, consistent with bonding, coordination number, and other energetically more important requirements. Neighboring atoms, of course, cannot approach each other so closely that their mutual overlap repulsions become large.

Another principle, applicable to crystal structures but not to glass structures, is that *there must be a motif that is periodically repeated* (in three dimensions for a three-dimensional crystal). Of course, the other structural principles must be obeyed where the motifs join together, as well as within each motif. A motif must have the same composition (atoms of the component elements in the same proportions) as the whole crystal. It must be electrically neutral. Because of the tendency for like atoms to be surrounded in like manner, the motif will usually be the smallest structural unit satisfying the requirements just mentioned, exceptions occurring only when other important principles cannot be satisfied by this smallest unit.

Structons in Silicate and Related Anions

The author now considers the application of the structon theory, together with the principles that have been outlined, to the structures of silicates and related compounds. To avoid trying to cover too much ground, the discussion will be limited to compounds in which the anions contain, in addition to oxygen, only Si, P, B, and/or Al atoms, tetrahedrally surrounded by the oxygens. Postponed for later consideration will be compounds in which these elements have coordination numbers other than 4, compounds in which the anions contain F atoms in place of (or in addition to) O atoms, and compounds containing hydrogen. Although not entirely neglecting the cations, the author will concentrate on the structures of the anions and neutral macromolecules, such as occur in the different forms of silica.

Both silicon and oxygen atoms have strong tendencies to have valence shells containing four electron pairs each. This is accomplished in silica and the silicates by sharing electron pairs. (If the bonds between a silicon atom and neighboring oxygen atoms have some double-bond character, more than four electron pairs are involved. For present purposes, the simpler assumption of one electron pair per silicon–oxygen bond seems preferable.) Because of the considerable difference between the electronegativities of silicon and oxygen,[33,34] Si–O bonds are much preferred over mixtures of Si–Si and O–O bonds. In agreement with these concepts, in silica[2] and in all known silicates[35-37] each Si atom is al-

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Table I
G Structons

Structural formula	$\overset{\displaystyle O}{\underset{\displaystyle O}{-O-G-O-}}$	$\overset{\displaystyle O}{\underset{\displaystyle O}{-O-G-O-}}$	$\overset{\displaystyle O}{\underset{\displaystyle O}{-O-G-O-}}$	$\overset{\displaystyle O}{\underset{\displaystyle O}{O-G-O-}}$	$\overset{\displaystyle O}{\underset{\displaystyle O}{O-G-O}}$
Condensed formula	$G(4O'')$	$G(O', 3O'')$	$G(2O', 2O'')$	$G(3O', O'')$	$G(4O')$
Shorthand symbol	G''''	G'''	G''	G'	G^0
Shorthand symbol	$--\overset{\shortmid}{\underset{\shortmid}{G}}--$	$--G\diagdown\diagup$	$--G--$	$G--$	G^0
Compositional formulas	PO_2^+ SiO_2 BO_2^- AlO_2^-	$PO_{5/2}$ $SiO_{5/2}^-$ $BO_{5/2}^{2-}$	PO_3^- SiO_3^{2-} BO_3^{3-}	$PO_{7/2}^{2-}$ $SiO_{7/2}^{3-}$	PO_4^{3-} SiO_4^{4-}
ϵ_{Si}, kcal/mol	3110	3123	3131	3137	3142

ways surrounded tetrahedrally by four oxygen atoms and each oxygen either bridges between two silicon atoms (O'') or is bonded to but one silicon (O'). (The O' nearly always and the O'' sometimes also have cation neighbors.) It should be noted that in silicon pyrophosphate, SiP_2O_7, each silicon atom apparently has six oxygen atoms around it.[38]

The Si–O bonds tie the atoms of these two elements together, in the silicates, into atomic groups or continuous networks, always negatively charged except in silica itself. Omitting consideration of the cations and neglecting, for the moment, the difference between bridging and nonbridging oxygens in the shell of atoms around silicon, the close-neighbor environment of the atoms in *the anions (and neutral network molecules)* can be described by stating that they *are composed of only structons represented by the formulas* $Si(4O)$, $O(2Si)$, *and* $O(Si)$. The relative numbers of these three types of structons in any given compound are readily computed from the formula, provided there are no silicons or oxygens other than those in the anions or neutral networks.

One may characterize the structon types further, *e.g.*, by specifying (1) that the oxygen atoms in the $Si(4O)$ structons surround the silicon atom tetrahedrally, with Si–O distances within a given range, (2) that the angles between the two O–Si bonds in the $O(2Si)$ structons are within a given range, (3) that the bond lengths in the $O(2Si)$ structons are normally longer than those in the $O(Si)$ structons,[39] and (4) that the oxygen atoms of the two types also have cation neighbors, specified, in any given case, as to kinds, numbers, orientations, and/or distances.

For the present such refinements will be neglected, but distinction will be made among five types of $Si(4O)$ structons, differing with regard to their numbers of bridging oxygens (O'') and nonbridging oxygens (O'). Distinction will also be made among corresponding types of other $G(4O)$ structons. (G is used to designate Si, P, B, or Al, in the anion or neutral network.) See Table I.

In the usual crystallographic terminology, these five structon types correspond to G-centered tetrahedra sharing 4, 3, 2, 1, and 0 corners, respectively, with other G-centered tetrahedra.

Calculations[40,41] of the energies required, for various crystalline silicates, to separate them completely into isolated monatomic ions (O^{2-}, Si^{4+}, Na^+, Ca^{2+}, etc.) have led to the values (ϵ_{Si}) for the Si structons listed in Table I. From these, it follows that two silicon structons of types that are not adjacent in the table are unstable, relative to an intermediate type. For example, if a silicon structon of type Si'''' reacts with one of type Si'' to give two of type Si''', there should be a decrease in the total energy (an increase in the sum of the ϵ_{Si} values), indicating an increase in stability. Assuming a similar relationship to hold for P and B structons, the following general principle is proposed. *Two* $G[(4 - i)O', iO'']$ *structon types (with the same G), in which i differs by more than one unit, will only rarely coexist.*

Density data for well-annealed sodium silicate glasses furnish evidence for this principle.[14-16] Straight-line relationships, with sharp breaks at the compositions of the individual structon types, when the specific volume is plotted against the weight fraction of SiO_2, are in agreement with the assumptions (1) that when the O/Si ratio is exactly the same as for one of the five types of Si structons, almost no structons of other types are present, and (2) that when the O/Si ratio is between the values of these ratios for two types of Si structons (at least when this ratio is less than 3), these two types are present, practically to the exclusion of all others. In these well-annealed glasses there are doubtless a few Si structons of other types present, and in glasses that are rapidly cooled from the molten state one would expect many more.

In crystals the limitations as to G structon types are even greater. Within the class of substances considered in this paper, the author has been able to find only one example (sodium triphosphate) of a crystal of known structure containing more than one of the five types of

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G structons (with the same G). The rarity of crystals with intermediate O/G ratios (hence, mixtures of G structon types) can be related to the near equivalence of the energies of anions containing two types of G structons in a given ratio but with different distributions of these two types and (for each distribution) different conformations. In triphosphate (P'-P''-P') and trisilicate (Si'-Si''-Si') anions only one distribution of the two structon types is possible and the number of conformations of essentially equal energy is relatively small (especially if cation distributions are taken into consideration), compared with those for more complex anions. For such more complex anions, one would expect that no single structure, satisfying the requirement for motif repetition in three dimensions, is much more stable than many other structures not satisfying this requirement. If the material is solidified by cooling from the molten state, the temperature range within which the anion structures become fixed is so high that different structon distributions of nearly the same energy will coexist in equilibrium with each other, and a glass, rather than a crystal, will be formed.[42-44]

On the basis of the foregoing, the following principle is proposed. *The G(4O) structons in a crystal will only rarely be of more than one type, for the same G, as regards the numbers of nonbridging and bridging oxygens.* If exceptions are found, it is predicted that they will be in crystals containing cations with strong attractions for nonbridging oxygens (cations of high charge or those which form "bonds" to the oxygens, having considerable covalent character) or in hydrates in which hydrogen atoms are bonded to nonbridging oxygens. It may be noted that mixtures of two G structon types, with the same G but different coordination numbers for the G atoms, do occur in crystals, for example, in some borates.

For later reference, another principle, based on obvious coulombic energy considerations, will be included here, even though it is rarely, if ever, applicable to crystals of the general class considered in this paper. If two types of G(4O) structons, for the same G but with different numbers of nonbridging and bridging oxygen neighbors, are present in a glass or crystal, *adjacent pairs of structons of one type and adjacent pairs of structons of the other type will rarely coexist.* These two kinds of pairs would tend to react together until one kind is used up. For example: $G'' \cdots G'' + G' \cdots G' \rightarrow 2G'' \cdots G'$. Exceptions would of course be expected in rapidly cooled glasses. Although no experimental evidence can be cited for this principle, the author believes it to be sound.

As shown in Table I, the formal charges on G atoms of different elements, when in structons of the same G(4O) class, are different. Because of this, the Coulomb energy is less, hence, the stability is greater, for two oxygen bridges between different G elements than for two oxygen bridges each connecting a pair of like G elements, other factors being equal. (This is equivalent to the argument that the coulombic repulsion between the G kernels tends to be minimized.) The author therefore proposes the following principle. *Two adjacent G structons, in which G represents one element, and two adjacent G structons, in which G represents another element, with the G structon types the same in one pair as in the other, will only rarely coexist.* This rule is observed in all crystal structures of which the author is aware except danburite,[45,46] $CaB_2Si_2O_8$, which contains both adjacent pairs of B'''' structons and adjacent pairs of Si'''' structons. This arrangement probably permits stronger bonding to the calcium ions than would be possible without this kind of pairing.

Let us consider a glass or crystal containing G structons of two or more types (G'''', G''', etc., Table I) and with G atoms of two or more different elements. How are the G elements preferentially distributed between the structon types? Since a nonbridging oxygen (O') has a greater effective negative charge than a bridging oxygen (O''), it would be expected that the *nonbridging oxygens* would *prefer to be attached to the* G *atoms of highest kernel charge:* P > Si > B or Al. (One might also consider this principle as a result of the tendency to minimize interkernel repulsions. Similar reasoning leads to the principle that lone electron pairs tend to be in the valence shells of atoms of highest kernel charge.)

The author knows of no crystal structures that would test this principle. It may, however, be useful in the analysis of future crystal structures and in dealing with glass structures.

It should be emphasized that the tendencies implied in the last five principles presented may sometimes be outweighed by other factors, such as the tendency to achieve the lowest possible energy of interaction between cations and anions, the tendency toward closest possible packing, and (in crystals) the geometrical requirements for a three-dimensionally repetitive structure.

Even though this paper is not primarily concerned with the arrangements of the *cations* in crystal structures, it may be noted that *a cation tends to have nonbridging, rather than bridging, oxygens as close neighbors.* This is presumably because of the greater effective negative charge on the former. Correspondingly, a *nonbridging oxygen,* in a crystal containing cations of different charge, *tends to have as close neighbors the cations of higher charge.* The extent to which these tendencies can be satisfied for any given crystal composition depends on the relative numbers of cations of each type and of oxygens of each type, coordination number limitations, geometric factors, etc.

The distinction between bridging and nonbridging oxygens is also important in dealing with the structures of hydrated compounds. *If the metal atoms in the cations are all of low charge, nonbridging oxygens will not usually exist in the presence of water molecules.* Hy-

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droxyl groups, each attached to one G atom, will be formed.

Because of these and other considerations, it is advantageous to distinguish, more than has often been done, between the nonbridging and bridging oxygen atoms and to consider how their numbers are related to the formula for the anion and to the relative numbers of cations of different types present.

Normalized Formulas, Charge Density, and Reticulation.—In dealing with the structon compositions of crystals and glasses, it is useful to represent the over-all chemical composition by a normalized formula, giving the relative numbers of the atoms of the component elements per G atom. For example, the normalized formula for a sodium calcium phosphosilicate has the form $Na_{na}Ca_{ca}(Si_{si}P_{1-si})O_\sigma$, with the subscripts here representing the appropriate numbers, integral or fractional. The subscript σ, rather than lower case "o," is used to avoid confusion with zero. The numerical values of the subscripts, like those in formulas of conventional type, must conform to the neutrality requirements; thus

$$na + 2ca + 4si + 5(1 - si) - 2\sigma = 0 \qquad (1)$$

The normalized formula for the corresponding macroanion is $(Si_{si}P_{1-si}O_\sigma)^{\rho-}$, where ρ, the *charge density function*, is the average negative charge per G atom in the anion. It is therefore also the sum of the positive charges on the cations, per G atom. For the compositions considered in this paper

$$\rho = 2\sigma - \bar{\nu}_G \qquad (2)$$

where $\bar{\nu}_G$ is the average kernel charge of the G atoms (5 for P, 4 for Si, 3 for B or Al).

The charge density function is important in theoretical considerations concerning properties such as hardness, heat of formation, and the relative stabilities of different configurations and conformations of the macroanions. These properties are also affected by the numbers, sizes, coordination numbers, and distributions of the cations and by partial covalent character of the bonding between some types of cations and oxygen atoms in the anions. To discuss these matters further here would carry us too far from the main theme of this paper. They are only mentioned to indicate the importance of the charge density function.

Another composition-dependent function, useful in dealing with rigidity and other physical properties, is the *reticulation function*, φ, measuring (when positive) the degree of branching or cross-linking in the anions. It is defined by the equation

$$\varphi = 2(\bar{z}_G - 1) - 2\sigma \qquad (3)$$

where $\bar{z}_G$ is the average coordination number of the G atoms. For the compositions here considered, z_G is always 4; hence

$$\varphi = 6 - 2\sigma \qquad (4)$$

For anions consisting of isolated rings or infinitely long chains, as when all G structons are of the G″ type, φ is

zero. If the average number of O″ atoms attached to a G atom is 3, as when all G structons are of the G‴ type, φ is unity. For a complete network, with all G structons of the G″″ type, φ is +2. Anions that are neither rings nor macroions have negative values of φ.

Assuming the principles that have been presented to be valid, one can deduce a great deal about crystal or glass structures merely from a knowledge of the over-all formula, especially if the formula for the anion is also known. In most cases the types of structons and the relative numbers of these types can be determined. For example, one can compute the numbers (σ', σ'') of O′ and O″ atoms (equal to the numbers of O(G) and O(2G) structons) per G atom from the equations

$$\sigma'' = 4 - \sigma \qquad (5)$$

and

$$\sigma' = 2\sigma - 4 \qquad (6)$$

These equations are easily derived from the requirement that the number of O′ (or O″) neighbors of G atoms must equal the number of G neighbors of O′ (or O″) atoms. If more than one G element and also (as is often the case in glasses) more than one type of G structon (G″″, G‴, etc.) are present, the distribution of G elements among the G structon types can usually be deduced from the assumed principle that nonbridging oxygens tend to be attached to the G atoms of highest kernel charge.

Knowing the structon types present in the anion, some of the other principles give information about the distribution of the structons of different types. Then, for crystals, the smallest structure motif conforming to that distribution is usually the correct one, provided that will permit satisfaction of the three-dimensional repetition requirement. The principles presented also lead to some deductions with regard to arrangement of the cations in the structure, though these deductions are sometimes less definite or less restrictive than for the anion structure.

Applications to Known Crystal Structures

Table II[47-90] lists the normalized formulas for many crystalline compounds of known structure, in the

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class here considered, with shorthand representations of the (experimental) structon compositions of the anions and values of σ', σ'', ρ, and φ, computed from eq 2–6. In most cases the anion structon compositions are uniquely determined by the principles presented here. These principles, however, do not enable one to determine (without considering cation distributions) whether an anion containing G structons that are all of the G″ type has a ring, zigzag, or other type of extended chain or a spiral chain structure, nor do the principles give (simply, at least) all of the details of the arrangement in network anions. Moreover, they do not determine the coordination numbers of elements (B, Al) of variable coordination number—a subject that the author hopes to deal with in another paper. Nevertheless, it is significant that none of the experimentally determined structures is in disagreement with the principles presented (with the possible exception of danburite, already discussed). On the basis of these results, one can proceed with confidence to use these principles to predict new crystal structures, to check tentative structures in the course of a crystal structure analysis, and to deduce arrangements of the atoms in glasses.

In accordance with the requirements here presented, all of the compounds having an O/G ratio, σ, of 2 have a three-dimensional network structure, with each G atom bridging to four others. This class includes all of the forms of silica, the feldspars, and some other silicate minerals, as well as certain aluminates and a high-temperature form of lithium borate.

In the aluminosilicate networks, containing both Si″″ and Al″″ structons, there seems to be a tendency for each Si″″ to be surrounded by only Al″″ neighbors, and *vice versa*, but the degree of ordering of this sort varies from mineral to mineral.[91] It is doubtless affected by the kinds and numbers of cations and by the temperature–time history during the solidification and annealing of the material. It may be remarked that even a very small excess of one of the two G elements (*e.g.*, silicon), randomly distributed in the network (or regularly distributed in some ways), might lead to a struc-

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ture composed of domains, each of regular structure—with completely regular alteration of the Al″″ and Si″″ structons—but so shifted relative to each other that the degree of ordering deduced from the X-ray data is much less than the true degree of ordering.

If all of the G structons are of the G″′ type, the principle of like surroundings for like atoms leads directly to a layer or sheet structure or to one that is cagelike. The simplest possible cage structure, having proper bond angles, is found in a metastable form of phosphorus pentoxide. The cages have the same structure as the molecules in the vapor state. Two other forms of this substance have sheet structures, as have the silicate anions in sodium disilicate (and in various other minerals, not listed because they are hydrated). The sheet structures seem to be favored for $GO_{5/2}$ anions, probably because they permit better satisfaction of the coulombic forces.

Amphiboles, which contain ladder-type polyanions with $\sigma = {}^{11}/_4$, are omitted from the table, since they are always hydrated.

With σ equal to 3, the G structons are all of the G″ type, connected together to form either rings or chains (ideally) of infinite length. Rings with less than three G″ structons (six ring atoms) are apparently unstable, doubtless because they would require bond angles that are too small. The infinite chains may be fully extended in a zigzag structure, as in the pyroxenes; they may be slightly less extended, as in β-wollastonite and one form (Maddrell's salt) of sodium metaphosphate; or they may be helical, as in two other forms (Kurrol's salt, α and β) of sodium metaphosphate and in silver and rubidium metaphosphates.

An isolated extended zigzag chain
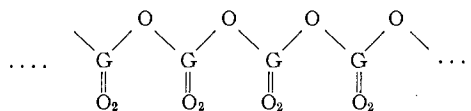
would tend to bend because the plane ($\cdots$) through the G atoms, perpendicular to the plane containing the G–O–G bridges, is not a symmetry plane. The forces on the two sides of this plane are not balanced. The bending may be prevented, however, by interactions with cations, producing a structure
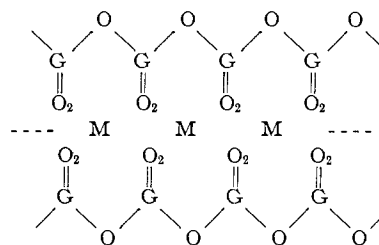
with a plane (or axes) of symmetry (----) and no unbalanced forces tending to produce bending. This is the situation in the pyroxenes. A similar situation exists with respect to the nonzigzag, nonhelical infinite chains in wollastonite and some of the polymetaphosphates.

When σ is greater than 3, there must be chain-ter-

TABLE II: NORMALIZED FORMULAS AND STRUCTURAL PARAMETERS

Structon compn of anion	Normalized formula	Name	σ'	σ''	ρ	φ	Ref
Si''''_∞	SiO_2	Quartz	0	2	0	2	2, 47
		Tridymite					48
		Cristobalite					49
$(Al''''_{1/4} Si''''_{3/4})_\infty$	$K_{1/4}Al_{1/4}Si_{3/4}O_2$	Sanidine	0	2	$1/4$	2	37
		Orthoclase					
		Microcline					
$(Al''''_{1/2} Si''''_{1/2})_\infty$	$Ca_{1/4}Al_{1/2}Si_{1/2}O_2$	Anorthite	0	2	$1/2$	2	50
$(Al''''_{1/2} Si''''_{1/2})_\infty$	$K_{1/3}Na_{3/3}Al_{1/2}Si_{1/2}O_2$	Nephelite	0	2	$1/2$	2	51
$(Al''''_{1/2} Si''''_{1/2})_\infty$	$K_{1/2}Al_{1/2}Si_{1/2}O_2$	Kalsilite	0	2	$1/2$	2	32
$(Al''''_{1/2} Si''''_{1/2})_\infty$	$Li_{1/2}Al_{1/2}Si_{1/2}O_2$	β-Eucryptite	0	2	$1/2$	2	52
$(Al''''_{1/2} Si''''_{1/2})_\infty$	$Na_{1/2}Al_{1/2}Si_{1/2}O_2$	α-Carnegieite	0	2	$1/2$	2	53
$(Al'''' Si'''')_\infty$	$Ca_{1/4}Al_{1/2}Si_{1/2}O_2$	Calcium aluminum silicate	0	2	$1/2$	2	30
$(Al'''' Si'''')_\infty$	$Ba_{1/4}Al_{1/2}Si_{1/2}O_2$	Barium aluminum silicate	0	2	$1/2$	2	62
$(B''''_{1/2} Si''''_{1/2})_\infty$	$Ca_{1/4}B_{1/2}Si_{1/2}O_2$	Danburite	0	2	$1/2$	2	45, 46
Al''''_∞	$NaAlO_2$	Sodium aluminate	0	2	1	2	54
Al''''_∞	$KAlO_2$	Potassium aluminate	0	2	1	2	55
Al''''_∞	$Ba_{1/2}AlO_2$	Barium aluminate	0	2	1	2	32
B''''_∞	$LiBO_2$	β-Lithium metaborate	0	2	1	2	56
P'''_∞	$PO_{5/2}$	Phosphorus pentoxide	1	$3/2$	0	1	57, 58
Si'''_∞	$NaSiO_{5/2}$	β-Sodium disilicate	1	$3/2$	1	1	59
P'''_4	$PO_{5/2}$	Phosphorus pentoxide	1	$3/2$	0	1	60
P''_∞	$LiPO_3$	Lithium metaphosphate	2	1	1	0	61
P''_∞	$NaPO_3$	Sodium metaphosphate	2	1	1	0	61, 63, 64
P''_∞	$RbPO_3$	Rubidium metaphosphate	2	1	1	0	65
P''_4	NH_4PO_3	Ammonium metaphosphate	2	1	1	0	66
P''_∞	$AgPO_3$	Silver metaphosphate	2	1	1	0	67
P''_4	$Al_{1/3}PO_3$	Aluminum metaphosphate	2	1	1	0	68
Si''_∞	Na_2SiO_3	Sodium meta-silicate	2	1	2	0	39
Si''_∞	$M^{II}SiO_3$	Pyroxenes	2	1	1	0	37
Si''_∞	$CaSiO_3$	Wollastonite	2	1	2	0	69, 70
Si''_∞	$Ca_{1/2}Mn_{1/2}SiO_3$	Bustamite	2	1	2	0	71
Si''_∞	$(Mn,Ca)SiO_3$	Rhodonite	2	1	2	0	72, 73
Si''_∞	$(Mn,Fe,Ca,Mg)SiO_3$	Pyroxmangite	2	1	2	0	74
Si''_6	$Be_{1/2}Al_{1/3}SiO_3$	Beryl	2	1	2	0	75
Si''_3	$Ba_{1/3}Ti_{1/3}SiO_3$	Benitoite	2	1	2	0	76
Si''_3	$K_{2/3}Zr_{1/3}SiO_3$	Wadeite	2	1	2	0	77
$P'--P''--P'$	$Na_{5/3}PO_{10/3}$	Sodium triphosphate	$8/3$	$2/3$	$5/3$	$2/3$	78
$P--P'$	$MgPO_{7/2}$	α-Magnesium pyrophosphate	3	$1/2$	2	-1	79
		β-Magnesium pyrophosphate	3	$1/2$	2	-1	80, 81
$P'--P'$	$CaPO_{7/2}$	β-Calcium pyrophosphate	3	$1/2$	2	-1	82
$P'--P'$	$Zr_{1/2}PO_{7/2}$	Zirconium pyrophosphate	3	$1/2$	2	-1	83
$Si'--Si'$	$CaMg_{1/2}SiO_{7/2}$	Åkermanite	3	$1/2$	3	-1	84
$Si'--Si'$	$ScSiO_{7/2}$	Thortveitite	3	$1/2$	3	-1	29
P^0	$Ba_{3/2}PO_4$	Barium orthophosphate	4	0	3	-2	85
Si^0	Be_2SiO_4	Phenacite	4	0	4	-2	86
Si^0	$(Fe,Mg)_2SiO_4$	Forsterite	4	0	4	-2	87
Si^0	$CaAl_{2/3}SiO_4$	Garnet	4	0	5	-2	88, 89
B^0	$MgAlBO_4$	Sinhalite	4	0	5	-2	90

minating structons of the G' type. The ions cannot be infinite in size, nor can they be rings—assuming like atoms to be bonded in like manner. For reasons that have been discussed, compositions with mixtures of G' and G'' structons do not readily crystallize (especially from the molten state), unless the relative proportions of these two types are such as to lead to only a single ionic composition. Sodium triphosphate is the only example, of known crystal structure, that the author has been able to find.

With σ equal to 3.5 and 4, the G structons are of the G' and G⁰ types, respectively. The anions are small and of the expected compositions and structures.

Conclusion

It has been shown that the structon concept, when applied in connection with other well-established struc-

tural principles, leads to conclusions in agreement with a large body of crystal structure knowledge. One can now confidently apply this concept and the procedures here outlined to crystals outside of the class included in the present treatment. One can also use them confidently to predict characteristics of the structures of crystals and glasses that have not yet been successfully analyzed experimentally.

Knowing the types of structons and the numbers of each type for many substances, one can now proceed to use this knowledge to compute the magnitudes of various properties by adding together the contributions to those properties of the different types of structons. It is predicted that considerably greater accuracy will be achieved in this way, for many properties, than by addition of the contributions of the individual atoms.

The Fluorination of Metal Stannates[1]

BY PETER J. MOEHS AND HELMUT M. HAENDLER[2]

The reaction of fluorine at about 500° with a series of anhydrous metal stannates has been studied. The resultant anhydrous fluorostannates are $MgSnF_6$, $CaSnF_6$, $SrSnF_6$, $BaSnF_6$, $CoSnF_6$, $NiSnF_6$, $CuSnF_6$, $ZnSnF_6$, $CdSnF_6$, $MnSnF_8$, and $PbSnF_8$. The hexafluorostannates contain the $SnF_6{}^{2-}$ anion, and X-ray diffraction and infrared spectroscopy have been used to postulate structures for some of these compounds.

Introduction

Studies of anhydrous fluorometalates of the general formula A_xBF_y have usually dealt with complexes in which A is an alkali metal or an ammonium ion, although a few alkaline earth, silver, and thallium complexes have also been studied. Babel[3] has recently reviewed the structural chemistry of octahedral fluoro complexes of the transition elements, and Wells[4] has discussed the general structural relationships.

Direct replacement of oxygen by fluorine at temperatures above 500° often proceeds smoothly and completely. The availability of many ternary oxides, A_mBO_n, offers a potential starting point for syntheses of anhydrous fluorometalates in which the type of A atom can vary widely. Many metal stannates can be prepared from readily available commercial products, and we have studied the complexes produced by direct fluorination of 11 of these. Formation of such anhydrous fluorostannates from aqueous solution or by direct reaction of tin(IV) fluoride and metal fluoride is not practical.

Experimental Section

Fluorination.—Samples of hydrated metal stannates, $MSnO_3 \cdot 3H_2O$,[5] were dehydrated at appropriate temperatures, as indicated by earlier thermal decomposition studies.[6] These temperatures are shown in Table I. Fluorine was generated in a Harshaw laboratory-type fluorine cell at an approximate rate of 2 l./hr and was passed through a Dry Ice and trichloroethylene trap and sodium fluoride scrubber at 100° to remove residual hydrogen fluoride. The fluorine was then passed into a heated nickel reaction chamber containing a nickel boat with the dehydrated stannate. Residual fluorine was destroyed in a soda lime scrubber.

Fluorine was first introduced at room temperature, and the sample temperature was then increased to 500° over a 1-hr period. The sample was cooled in fluorine, the fluorine was purged with nitrogen, and the product was removed, pulverized, and then refluorinated for about 30 min at 500°. Fluorination was repeated three or four times. The products were subsequently handled in a nitrogen atmosphere.

Analysis.—Fluorine was determined by oscillometric titration[7] after distillation in the Tenso-Lab apparatus.[8]

Tin was determined by atomic absorption spectrometry, using a Techtron AA-3 unit, with the tin resonance line at 2863 Å.[9] A tin concentration range of 200–1000 ppm was used for all analyses. Standards and samples were dissolved in 0.5 M hydro-

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(2) To whom communications should be addressed.
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