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Stoichiometry and Local Atomic Arrangements in Crystals[1]

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Valence crystals have bulk stoichiometries that are electroneutral with respect to formal atomic valence, and structures in which cation sites are formed entirely by anions and vice versa. This description is shown to be equivalent to a set of stoichiometric and structural rules limiting local atomic configurations in valence crystals. Algebraic equivalents of these rules are used to derive a necessary mathematical link between bulk stoichiometry and local atomic arrangements in valence crystals. In the limit of no charge imbalances on anion sites, this link reduces to the electrostatic valence principle of Pauling. Numerical analysis shows that limits upon the coordination numbers of cations and anions severely restrict the number and type of local configurations that could ever be combined to form an electroneutral bulk stoichiometry, regardless of the valence of the anion or the magnitude of charge imbalances on anion sites. © 1991 Academic Press, Inc.

I. Introduction

All representations of the bulk stoichiometry of a well-ordered crystal are equivalent within a factor of a rational number because they are derived from the frequency of appearance of an atom or site in the crystal structure. Since a minimum representation of crystal structure, such a a unit cell, is a complete description of a well-ordered crystal, then in some sense crystal structure *determines* stoichiometric representations; for example, investigators can use high-quality X-ray diffraction data to estimate bulk stoichiometries of unknown materials. On the other hand, bulk stoichiometry generally does not limit crystal structure because while well-constrained rules proscribe local atomic arrangements in a crystal, no equivalent set proscribes stoichiometry.

Empirically, however, one sees patterns linking aspects of crystal stoichiometry and structure. An interesting, if extremely simple, observation is that crystal bulk stoichiometries are often electroneutral with respect to the formal valences of their components. Examples include most simple halides and oxides, nitrates, sulfates, perchlorates, phosphates, and the majority of simple sili-

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cates. This "electroneutral condition" is taken as a basic rule governing aspects of structure in such crystals. If it is also required that all cations are surrounded solely by anions and vice versa, one obtains a useful algebraic link between local atomic configurations and stoichiometry.

This algebraic link is drawn from consideration of valence and coordination number alone, two of many factors determining the relative stabilities of crystal structures. We take no account of the magnitude of bonding interactions between atoms, interatomic separations, bond angles, or other metric properties of crystals. This method cannot be used to determine atomic positions in a unit cell, lattice energies, or any bulk thermodynamic properties. On the other hand, with this approach one can calculate all possible local atomic configurations consistent with a given electroneutral bulk stoichiometry. Since this produces many more possibilities than those realized in nature, one has a tool with which to explore factors determining the stabilities of crystals. The reader will recognize the debt this approach owes to the classic study by Pauling (*1*), as well as more recent works by Baur (*2*), Brown, Shannon, and others (*3–5*), O'Keeffe and others (*6–8*), and Burdett and McLarnan (*9*), and the analysis of the symbolic content of stoichiometry of Hoppe (*10*).

We first develop the empirical arguments and rationalizations upon which this study is based and express them as three rules. The rules are cast as algebraic expressions and convoluted together to obtain a general expression explicitly linking stoichiometry and local atomic arrangements in crystals with electroneutral stoichiometries, referred to as the Neutral Structural Criterion. The Neutral Structural Criterion is used to show the *equivalence* of cationcentric and anioncentric descriptions of crystal structure and that neither is a *sufficient description,* and also that the electrostatic valence principle of Pauling (*1*) is simply a limiting case of the more general condition. Last, structure and stoichiometry are analyzed numerically for a single anion site to determine how various factors limit the local structures of electroneutral crystals.

II. Formalism

Simple representations of bulk stoichiometry often ignore distinctions between crystallographically distinct sites, especially when the same atom appears in several different sites. We are less concerned with the identities of atoms per se than with the sites they occupy or form and so will take entries in a stoichiometric formula as *sites*. The stoichiometric coefficients of sites are proportional to their number in the unit cell and thus are rational numbers. Therefore, we lose no information by requiring that all sites in a formula unit be integrally represented. We say that the electroneutral condition is satisfied when the sum of valences of all atoms in a formula unit is zero. Thus any collection of atoms that is a rational number multiple of an electroneutral bulk stoichiometry must be electroneutral, regardless of the relationships between individual atoms. This mathematical convenience in no way restricts the actual types of bonding forces, the scale over which they act, or the scale over which electroneutrality is obtained. Indeed, instead of viewing stoichiometry as a consequence of valence—perhaps implying ionic bonding forces—one might view valence to be a consequence of stoichiometry, an interpretation paralleling the historic development of the concept of valence.

This description of bulk electroneutrality tacitly assumes that a distinction can be made between positively charged *cations* and negatively charged *anions,* whether or not such a distinction has any physical significance. In fact, crystals with electroneutral stoichiometries tend to have cation coordination polyhedra formed entirely by anions and vice versa. The whole number representing the number of atoms of *opposite polarity* surrounding a central atom in a site is referred to as the *coordination number* of the site. When atoms of the same polarity are nearest neighbors, as in some chalcogenides or crystal structures based on cation packing (*8*), one usually does not find electroneutral stoichiometries, so these are excluded from consideration. This definition of coordination number does not mean *bonding interactions* in crystals are solely between cations and anions—it does not reference bonding interactions at all.

Coordination number is an interesting structural parameter because it often remains nearly constant with variations in bond lengths and angles. This means actual geometric relationships between atoms cannot be obtained from coordination number alone. On the other hand, bond length and angles bear no necessary relationship to bulk stoichiometry, but there is a necessary and very important link between coordination number and structure—there is a 1 : 1 correspondence between changes in the coordination numbers of cations and anions. If an anion far from a certain cation is included in the coordination polyhedron of the cation, then the coordination numbers of both are increased. Each cation–anion bond implies an anion–cation bond, so the sum of the coordination numbers of all anion sites, each weighted by the appropriate stoichiometric coefficient, must equal the weighted sum of the coordination numbers of all cation sites.

We arrive at three rules, taken as the defining properties of *valence crystals:*

(R1) It must be possible to distinguish between cations and anions;

(R2) The weighted sum of all cation valences exactly compensates the weighted sum of all anion valences;

(R3) The weighted sum of all cation coordination numbers must equal the weighted sum of all anion coordination numbers.

TABLE I

Typography and Symbology

Ai	A label signifying a unique cation site
a_i	Integral stoichiometric coefficient of Ai
K	A general site (cation or anion)
i	The index for cation sites
j	The index for anion sites
m	The number of unique cation sites
n	The number of unique anion sites
$n(K)$	The coordination number of (the atom in) site K
$N_K(K')$	The number of times the atom in K' appears around the atom in site K (Eq. (9))
X_j	A label signifying an unique anion site
x_j	Integral stoichiometric coefficient of X_j
$Z(K)$	The valence of atom K
$Z_s(K)$	The site valence of K, or the sum of bond strengths of all atoms that form site K (see Eq. (12))
α_i	The number of bonds between the a_i cations Ai and surrounding anions (see Eq. (5))
ξ_j	The number of bonds between the x_j anions X_j and surrounding cations (see Eq. (5))
$\delta(K)$	The charge imbalance on site K; the difference between the site valence of K and the valence of the atom occupying K (see Eq. (16))
$\sigma(K)$	The bond strength of K (see Eq. (6))
$\omega(A, B)$	The number of solutions to Eq. (19) involving cations of valence $Z(A)$ and $Z(B)$
$\Omega(A)$	The number of solutions to Eq. (19) involving one or more cations of valence $Z(A)$ and cations of any other valence (see Eq. (20))

III. Algebraic Description of Valence Crystals

R1, R2, and R3 are cast as algebraic expressions: the typography employed here and elsewhere in this study is summarized in Table I. From R1, valence crystal stoichiometries are written

$$A1_{a1}A2_{a2}\ldots Am_{am}X1_{x1}X2_{x2}\ldots Xn_{xn}. \quad (1)$$

Cations and anions are referenced by the labels Ai and Xj, respectively, and a_i and x_j are their (integer) stoichiometric coefficients; the index i applies solely to cations or cation sites and the index j to anions or anion sites. m and n are the total numbers of unique cation and anion sites, respectively; for now it is not necessary to adopt criteria specifying precisely what makes a site "unique" save that it is explicit in bulk stoichiometry. For R2, the electroneutral condition, we introduce an operator, $Z(K)$, which returns the valence of the atom in site K:

$$\sum_{i=1}^{m} a_i Z(Ai) + \sum_{j=1}^{n} x_j Z(Xj) = 0. \quad (2)$$

R3 is recast using an operator that returns the coordination number of K, $n(K)$,

$$\sum_{i=1}^{m} a_i n(Ai) = \sum_{j=1}^{n} x_j n(Xj). \quad (3)$$

Equation (3) links bulk stoichiometric constraints, the stoichiometric coefficients a_i and x_j, with structural constraints, the coordination numbers $n(K)$.

Equations (2) and (3) are convolved together as

$$\sum_{i=1}^{m} \frac{\alpha_i Z(Ai)}{n(Ai)} + \sum_{j=1}^{n} \frac{\xi_j Z(Xj)}{n(Xj)} = 0, \quad (4)$$

where

$$\alpha_i = a_i n(Ai) \quad \text{and} \quad \xi_j = x_j n(Xj). \quad (5)$$

α_i is equivalent to the number of bonds formed between all a_i of the cations in sites Ai and surrounding anions, and ξ_j the number of bonds formed between all x_j anions Xj and surrounding cations. $Z(K)$ and $n(K)$ are unique properties of the atom in site K and so can be combined into a new operator,

$$\sigma(K) = \frac{Z(K)}{n(K)}. \quad (6)$$

By analogy with Pauling (*1*), $\sigma(K)$ is referred to as the *bond strength* of the atom in site K. Substituting appropriate expressions for $\sigma(K)$ into Eq. (4) yields

$$\sum_{i=1}^{m} \alpha_i \sigma(Ai) + \sum_{j=1}^{n} \xi_j \sigma(xj) = 0. \quad (7)$$

Equation (7) states that *the sum of all cation bond strengths exactly compensates the sum of all anion bond strengths in a valence crystal.* From Eq. (2),

$$\sum_{i=1}^{m} \alpha_i \sigma(Ai) = \sum_{i=1}^{m} a_i Z(Ai) \quad \text{and}$$

$$\sum_{j=1}^{n} \xi_j \sigma(xj) = \sum_{j=1}^{n} x_j Z(Xj), \quad (8)$$

meaning sums of bond strengths taken over all bonds are exactly equivalent to sums of valences taken over all atoms in the stoichiometric formula (Brown (*5*) examines this statement in a somewhat different context).

Bond strength "normalizes" the valence of an atom to the site it occupies, but still provides no information about the atoms that *form* the site. A more useful algorithm would assign all atoms to specific sites, fixing the relationships between each atom and all of its neighbors—one may think of this as essentially fixing the "composition" of a site. To this end, we introduce an operator, $N_K(K')$, which returns the number of times the atom K' appears in the coordination polyhedron of K. We can use $N_K(K')$ to obtain the coordination number of K:

$$\sum_{j=1}^{n} N_{Ai}(Xj) = n(Ai) \quad \text{and}$$

$$\sum_{i=1}^{m} N_{Xj}(Ai) = n(Xj). \quad (9)$$

Since each Ai–Xj bond requires an Xj–Ai bond,

$$a_iN_{Ai}(Xj) = x_jN_{Xj}(Ai).$$

With this operator, the sum of bond strengths of the anions that form site Ai is

$$\sum_{j=1}^{n} N_{Ai}(Xj)\sigma(Xj),$$

which when taken over all cation sites is

$$\sum_{i=1}^{m} a_i \sum_{j=1}^{n} N_{Ai}(Xj)\sigma(Xj).$$

We see in comparison with the relations in Eq. (8) that

$$\sum_{i=1}^{m} a_i \sum_{j=1}^{n} N_{Ai}(Xj)\sigma(Xj) = \sum_{j=1}^{n} \xi_j\sigma(Xj) = \sum_{j=1}^{n} x_jZ(Xj) \qquad (10a)$$

and likewise for cations about anion sites that

$$\sum_{j=1}^{n} x_j \sum_{i=1}^{m} N_{Xj}(Ai)\sigma(Ai) = \sum_{i=1}^{m} \alpha_i\sigma(Ai) = \sum_{i=1}^{m} a_iZ(Ai). \qquad (10b)$$

Substituting the leftmost expressions in Eqs. (10a) and (10b) into Eq. (2) yields

$$\sum_{i=1}^{m} a_i \sum_{j=1}^{n} N_{Ai}(Xj)\sigma(Xj) + \sum_{j=1}^{n} x_j \sum_{i=1}^{m} N_{Xj}(Ai)\sigma(Ai) = 0. \qquad (11)$$

Equation (11) intimately links bulk stoichiometric coefficients of atoms *occupying* sites with the numbers and types of atoms *forming* sites. It is obtained directly from R1, R2, and R3, and therefore is a fundamental property of any valence crystal. We refer to it as the Neutral Structure Criterion.

The frame of reference of the Neutral Structure Criterion is quite different from that of the electroneutral condition, Eq. (2). For example, in Eq. (2) the cation stoichiometric coefficients a_i are multiplied by $Z(Ai)$, resulting in a sum that is a positive integer. In Eq. (11), however, the a_i are multiplied by a sum of negative rational numbers, but the resulting summation over all cation sites is a negative integer (Eq. (10a)). Because of this, each of the innermost summations in Eq. (11) is much like a "charge" on a site, or a *site valence, $Z_s(K)$,* that counters the valence of the atom in the site:

$$Z_s(Ai) = \sum_{j=1}^{n} N_{Ai}(Xj)\sigma(Xj) \quad \text{and} \quad Z_s(Xj) = \sum_{i=1}^{m} N_{Xj}(Ai)\sigma(Ai). \qquad (12)$$

The *sign* of site valence is always known—it is the opposite that of the atom occupying the site—but its magnitude is a property of the number and valences of atoms that form the site and is therefore a unique property of the crystal structure. Since site valence is a rational number, *atomic valence need not be compensated by site valence.* Comparison with Eqs. (10a) and (10b) yields the important equalities

$$|\sum_{i=1}^{m} a_iZ_s(Ai)| = |\sum_{j=\mathrm{i}}^{n} x_jZ_s(Xj)| = |\sum_{i=1}^{m} a_iZ(Ai)| = |\sum_{j=1}^{n} x_jZ(Xj)|. \qquad (13)$$

These show that site and atomic valence formalisms are equivalent. Site valence is a fundamental and necessary property of any valence crystal; however, it may not be the only operator that could satisfy the equalities in Eq. (13). For example, Brown and Shannon (*4*) cast bond strength as a function of empirically determined ionic radii and employ these to satisfy a relationship analogous to Eq. (11). Such approaches require metric constraints beyond the scope of the present model and are not considered further.

The unusual reference frame of the Neutral Structure Criterion is best illustrated by an example, here the mineral forsterite

Mg_2SiO_4 (*11*). Ignoring distinctions between the various crystallographic sites, Mg sites are formed by 6 oxygen ($\sigma(\mathrm{Mg}) = +2/6$), Si sites by 4 oxygen ($\sigma(\mathrm{Si}) = +4/4$), and oxygen sites by 3 Mg and 1 Si ($\sigma(\mathrm{O}) = -2/3 + 1$)):

$$
\begin{aligned}
Z_s(\mathrm{Mg}) &= N_{\mathrm{Mg}}(\mathrm{O})\sigma(\mathrm{O}) = 6(-2/4) = -3 \\
Z_S(\mathrm{Si}) &= N_{\mathrm{Si}}(\mathrm{O})\sigma(\mathrm{O}) = 4(-2/4) = -2 \\
Z_s(\mathrm{O}) &= N_{\mathrm{O}}(\mathrm{Mg})\sigma(\mathrm{Mg}) + N_{\mathrm{O}}(\mathrm{Si})\sigma(\mathrm{Si}) \\
&= 3(+2/6) + 1(4/4) = +2.
\end{aligned}
$$

Substituting these into Eq. (11),

$$
\begin{aligned}
&a_{\mathrm{Mg}}Z_s(\mathrm{Mg}) + a_{\mathrm{Si}}Z_s(\mathrm{Si}) + x_{\mathrm{O}}Z_s(\mathrm{O}) \\
&\quad = 2(-3) + 1(-2) + 4(+2) = 0,
\end{aligned}
$$

verifying the premise that forsterite is a valence crystal. If this calculation is performed for each crystallographically distinct Mg and O site the same result is obtained, but the complexity of the analysis increases.

IV. Local Environments in Valence Crystals

Equation (10) could be used to determine all local arrangements of cations and anions consistent with the bulk stoichiometry of any valence crystal, but this typically produces a large number of possibilities for all but the simplest bulk stoichiometries. Note that each term in the summations in Eq. (10) refers to a distinct site, and only when sites are considered collectively does one impose the condition of electroneutrality. This suggests determining all possible *local* atomic arrangements and then combining sets of related solutions (containing, for example, the same set of cations and anions occupying the same set of sites) to determine whether or not an electroneutral bulk stoichiometry can result.

An implicit consequence of Eq. (10) is that knowledge of the "compositions" of, say, all cation sites largely determines the possible local atomic configurations of a valence crystal, as certain properties unique to anion sites are explicitly part of the description of cation sites, and vice versa. Consider, for example, algorithms derived from Eq. (10) for the stoichiometric coefficients of cation and anion sites. From Eq. (7), the number of bonds between the a_i cations in site *Ai* and *all* anions is

$$a_i n(Ai) = \sum_{j=1}^{n} x_j N_{Xj}(Ai);$$

thus

$$a_i = \frac{1}{n(Ai)}\sum_{j=1}^{n} x_j N_{Xj}(Ai) \quad \text{and}$$

$$x_j = \frac{1}{n(Xj)}\sum_{i=1}^{m} a_i N_{Ai}(Xj). \qquad (14)$$

In the example of forsterite considered above,

$$
\begin{aligned}
a_{\mathrm{Mg}} &= \left(\frac{1}{n(\mathrm{Mg})}\right)(x_{\mathrm{O}}N_{\mathrm{O}}(\mathrm{Mg})) = (1/6)(4)(3) \\
&= 2, \\
a_{\mathrm{Si}} &= \left(\frac{1}{n(\mathrm{Si})}\right)(x_{\mathrm{O}}N_{\mathrm{O}}(\mathrm{Si})) = (1/4)(4)(1) \\
&= 1, \\
a_{\mathrm{O}} &= \left(\frac{1}{n(\mathrm{O})}\right)[a_{\mathrm{Mg}}N_{\mathrm{Mg}}(\mathrm{O}) + a_{\mathrm{Si}}N_{\mathrm{Si}}(\mathrm{O})] \\
&= (1/4)[(2)(6) + (1)(4)] = 4
\end{aligned}
$$

(valence need not be considered because the bulk stoichiometry is electroneutral). We see that descriptions of cation sites and anion sites are mutually dependent; the distinction between cations and anions in valence crystals is both necessary and real. Moreover, a cationcentric approach to valence crystal structure—i.e., considering cation coordination polyhedra alone—is no more descriptive or meaningful than an anioncentric approach.

If the positions of all cations in a valence crystal are known, then everything about the anion sites is known except the identities of the anions within them. If there are k distinguishable anions, this leaves at most $k!$ different distributions of anions over anion sites. In real crystals there tend to be fewer distinguishable anions than anion sites, so the number of unique configurations is still smaller. Only one type of anion (e.g., oxygen) is present in many valence crystals, so in these knowledge of the distributions of cations over the anion sites completely determines the valence crystal structure.

IV.A. Individual Cation and Anion Sites

From Eq. (11), local arrangements of cations about anions must satisfy

$$\sum_{i=1}^{m} a_i \sum_{j=1}^{n} x_j N_{Xj}(Ai)\sigma(Ai) + \sum_{j=1}^{n} x_j Z(Xj) = 0. \quad (15)$$

By definition (Eq. (12)), the innermost summation in the left-hand term of Eq. (15) is the site valence of the anion site X_j. We have shown that $Z_s(Xj)$ need not exactly compensate $Z(Xj)$. Therefore a description of the local environment of the atom in site K requires a new operator, $\delta(K)$, which returns the difference between $Z_s(K)$ and $Z(K)$. For a single anion site

$$\sum_{j=1}^{n} x_j N_{Xj}(Ai)\sigma(Ai) + Z(Xj) = \delta(Xj). \quad (16)$$

When $\delta(Xj) \geq 0$ then $Z_s(Xj)$ overcompensates $Z(Xj)$, and the anion is said to be *overbonded;* when $\delta(Xj) \leq 0$ then $Z_s(Xj)$ undercompensates $Z(Xj)$, and the anion is *underbonded.* In the analogous relationship for cations,

$$\sum_{i=1}^{m} a_i N_{Ai}(Xj)\sigma(Xj) + Z(Ai) = \delta(Ai); \quad (17)$$

negative values of $\delta(Ai)$ mean the cation is overbonded, and positive values mean the cation is underbonded. As the example of forsterite shows, it is quite possible that all anions might occupy charge-compensated sites while all cations occupy underbonded or overbonded sites, and vice versa.

Finally, from application of the equalities in Eq. (13),

$$\sum_{j=1}^{n} x_j \delta(Xj) = 0 \quad \text{and} \quad \sum_{i=1}^{m} a_i \delta(Ai) = 0. \quad (18)$$

Equation (18) requires the sum of charge imbalances over all cation sites and the sum over all anion sites to be exactly zero. *Cation or anion charge imbalances can only be compensated by charge imbalances of opposite sign on other cation or anion sites, respectively.* This point is illustrated by the chain silicate mineral hedenbergite, $CaFeSi_2O_6$ (*12*). Cation coordination numbers are n(Ca) = 8, n(Fe) = 6, and n(Si) = 4. There are three oxygen sites:

$O_1 = 2Fe + 1Ca + 1Si$:

$$Z_s(O1) = 2(\tfrac{2}{6}) + 1(\tfrac{2}{8}) + 1(\tfrac{4}{4}) = +1\tfrac{11}{12}$$

$O_2 = 1Fe + 1Ca + 1Si$:

$$Z_s(O1) = 1(\tfrac{2}{6}) + 1(\tfrac{2}{8}) + 1(\tfrac{4}{4}) = +1\tfrac{7}{12}$$

$O_3 = 2Ca + 2Si$:

$$Z_s(O1) = 2(\tfrac{2}{8}) + 2(\tfrac{4}{4}) = +2\tfrac{1}{2}$$

$$\sum_{j=1}^{3} \delta(O_j) = \sum_{j=1}^{3} [Z(O_j) + Z_s(O_j)] = 3(-2) + [+1\tfrac{11}{12} + 1\tfrac{7}{12} + 2\tfrac{1}{2}] = 0.$$

Although none of the oxygen atoms is charge compensated by its site valence, the sum of $\delta(O_j)$ taken over all distinct oxygen sites is zero; thus hedenbergite is a valence crystal. Equation (18) also applies to the cation sites:

$Ca = 2(O_1 + O_2 + 2O_3)$:

$$Z_s(Ca) = 2[-\tfrac{2}{4} - \tfrac{2}{3} - 2(\tfrac{2}{4})] = -4\tfrac{1}{3}$$

$Fe = 2(2O_1 + O_2)$:

$$Z_s(Fe) = 2[-2(\tfrac{2}{4} - \tfrac{2}{3}] = -3\tfrac{1}{3}$$

$$2\mathrm{Si} = 2(\mathrm{O}_1 + \mathrm{O}_2 + 2\mathrm{O}_3):$$
$$Z_s(\mathrm{Ca}) = 2[-\tfrac{2}{4} - \tfrac{2}{3} - 2(\tfrac{2}{4})] = 2(-2\tfrac{1}{6})$$

$$\sum_{i=1}^{4} \delta(Ai) = \sum_{i=1}^{4} [Z(Ai) + Z_s(Ai)]$$
$$= (2 + 2 + 2(4)) + [-4\tfrac{1}{3} - 3\tfrac{1}{3} - 4\tfrac{1}{3}] = 0$$

(notice that the magnitudes of charge imbalances on the oxygen sites are much smaller than those on the cation sites). The relations in Eq. (18) are general to any material satisfying R1, R2, and R3; for example, it must be satisfied in silicate glasses, although possibly over many more atoms than in a simple crystal.

IV.B. The Electrostatic Valence Principle

In the special case that $\delta(Xj)$ is zero, Eq. (17) is written

$$\sum_{i=1}^{m} a_i N_{Ai}(Xj)\sigma(Xj) + Z(Ai) = 0.$$

This is essentially the *electrostatic valence principle* of Pauling (*1*) expressed as an equality. We restate the principle in terms of the present model: *in the most stable valence crystals anion site valences tend to compensate anion valences.* As seen above, this is not generally true for cation sites, suggesting the following extension:

> *The most stable valence crystal structures minimize charge imbalances on anion sites relative to alternative structures, even at the expense of overbonding and underbonding cations.*

In this extension, the bonding requirements of anions are seen as a driving force underlying the most stable crystalline form of a given bulk stoichiometry. As with the electrostatic valence principle, one need not look far to find exceptions to this statement, exceptions which clearly point to factors beyond simple electrostatics that affect the relative stabilities of crystals.

V. Parameters Limiting Valence Crystal Structures

The summations in Eqs. (16) and (17) are bounded by geometric limits on cation and anion coordination numbers. Furthermore, the value of $\delta(K)$ for any particular cation or anion site has a special relationship to values of $\delta(K)$ for other cation/anion sites because, from Eq. (18), charge imbalances on all cation sites and on all anion sites must each sum to zero. Moreover, there is a practical limit for values of $\delta(K)$, which for anions is $Z(Xj) < \delta(Xj) < Z_s(Xj)$. We now consider a numerical analysis of how these limits impact the number and types of local atomic configurations in valence crystals. This is performed using a variant of Eq. (16) for the valence crystal stoichiometry $A_aB_bX_x$, where A and B are cations with unique valences and/or coordination numbers, and X is an anion of fixed valence. The minimum and maximum coordination numbers of atom K, $n_{\min}(K)$ and $n_{\max}(K)$, are such that

$$n_{\min}(Ai) \le \sum_{j=1}^{n} N_{Ai}(Xj) \le n_{\max}(Ai) \quad \text{and}$$
$$n_{\min}(Xj) \le \sum_{i=1}^{m} N_{Xj}(Ai) \le n_{\max}(Xj).$$

We adopt fixed limits for the magnitude of charge imbalances on anions and represent these as $\delta_{\max}(Xj)$—for the present purposes these are empirical and therefore arbitrary. From Eq. (16) we require that

$$\left|\sum_{j=1}^{n} x_j N_{Xj}(Ai)\sigma(Ai) + Z(Xj)\right| \le \delta_{\max}(Xj).$$

We will further require that each anion site be formed by at least one each of cations A and B; hence the minimum anion coordination number, $n_{\min}(X)$, is 2. Since $\delta_{\max}(Xj)$ represents a range rather than a specific value, most combinations of cation valences $Z(A)$ and $Z(B)$ will produce several "acceptable" trial local configurations—the total number of acceptable trial solutions is $\omega(A, B)$. Variations in $\omega(A, B)$ are examined as a function of $Z(X)$; $n_{\max}(A)$, $n_{\max}(B)$, and $n_{\max}(X)$; and $\delta_{\max}(Xj)$. The appropriate form of Eq. (16) is

$$\frac{N_X(A)Z(A)}{n(A)} + \frac{N_X(B)Z(B)}{n(B)} - \delta(X) + Z(X) = 0 \quad (19)$$

(the subscript j is omitted because a single anion site is considered).

This model produces variations in the number of trial solutions, $\omega(A, B)$, with changes in the limiting constraints that are qualitatively the same as those in models involving more cation or anion sites. This might be inferred from the equalities in Eq. (13), which show that sums over site valences and atomic valences have the same magnitude. Unlike a sum of integral atomic valences, site valence is a sum of rational numbers, so increasing the number of terms in the summation produces relatively few additional solutions likely to satisfy the Neutral Structure Criterion (Eq. (11)). On the other hand, brute-force analysis of Eq. (19) yields many trial configurations that cannot be found in valence crystals. Thus, $\omega(A, B)$ increases with the number of cations surrounding an anion, but the number of realistic solutions does not increase strongly.

This model is also useful because many valence crystals have only two cation sites with distinct coordination numbers or that are occupied by cations with distinct valences. This set includes valence crystals of the bulk stoichiometry $A_aB_bC_cX_x$, in which the cation C is surrounded by a fixed number of X atoms (e.g., Si in low-pressure silicates, C in carbonates). The cation C makes a static contribution to anion site valence and reduces the sum of bond strengths required from cations A and B. In these cases, the effective valence of the anion, $Z(C) + \sigma(C)$, is as valid an expression of anion valence as $Z(X)$ itself.

Initial limits for cation and anion coordination numbers and the value of $\delta_{\max}(Xj)$ are summarized in Table II. Cation valences range from +1 to +6 and anion valences are either −1 or −2. Cation coordination numbers are initially constrained to the range from 2 to 12, where the former is a minimum for a linearly repeating unit cell and the latter the coordination number of a hard sphere in a close-packed array. Anion coordination numbers must range from 2 to 8, the former observed in low-pressure polymorphs of SiO_2, the latter close to the upper limit for oxygen in real crystals (*8*). To compare $\omega(A, B)$ for anions of different valences, $|\delta_{\max}(Xj)| \leq 0.5$, regardless of the valence of the anion. Several oxyanions of high-valence cations show spectacular excursions from this range, such as interior oxygen atoms in the 12- and 18-phosphotungstate ions, $PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{6-}$ (*13*), which obviously indicate that forces other than electrostatics are important in bonding arrangements. Baur (*2*) has shown that even simple oxides or crystals of simple oxyanions show values of $\delta(X)$ as great as 40% of the valence of oxygen. In short, "real" local configurations for −1 anions are probably well represented, but real solutions for −2 anions are underrepresented.

Table III shows solutions to Eq. (19) subject to the limits $n_{\min}(X) = 2$, $n_{\max}(X) = 6$, $n_{\max}(A) = n_{\max}(B) = 10$, and $\delta_{\max}(X) = 0$, for combinations of +2 cations arranged about a −1 anion. Note that multiple solutions are obtained even though these limits are stricter than those used elsewhere in this analysis. Also, when $Z(A) = Z(B)$ and $n(A) = n(B)$ the sites are considered indistinguishable and are counted only once. Last, some solutions produce cation sites with strikingly different coordination numbers. $\omega(2, 2)$ for these conditions is just the total number of solutions in Table III, or 11.

TABLE II

INITIAL LIMITS FOR CALCULATING LOCAL CONFIGURATIONS

Range of cation valences	$+1 \leq Z(A), Z(B) \leq +6$
Range of anion valences	$Z(X) = -1$ or -2
Minimum and maximum cation coordination numbers	$n_{\min}(A) = n_{\min}(B) = 2$, $n_{\max}(A) = n_{\max}(B) = 12$
Minimum and maximum anion coordination numbers	$n_{\min}(X) = 2$, $n_{\max}(X) = 8$
Range of charge imbalances on anion sites	$\lvert\delta_{\max}(X)\rvert \leq 0.5$

VI. Limiting Parameters and Local Atomic Arrangements

Table IV shows the number of trial configurations, $\omega(A, B)$ for -1 and -2 anions subject to the initial limits (Table II). It is convenient to represent the total number of solutions involving cations of valence $Z(A)$ with cations of all other valences as $\Omega(A)$:

$$\Omega(A) = \sum_{b=+1}^{+6} \omega(A, b). \tag{20}$$

$\Omega(A)$ are shown at the bottom of each column in Table IV. The distinction between cation sites A and B is arbitrary, so $\omega(A, B)$ must equal $\omega(B, A)$ (the latter are shown in parentheses for -1 anions and are omitted in the remaining tables). This and the indistinguishability of cations of the same valence explains low values of $\omega(A, B)$ when $Z(A) = Z(B)$. The total number of solutions for a cation of valence $Z(A)$, $\Omega(A)$, decreases steadily with increasing valence of the cation for -1 anions, but shows a local maximum for solutions involving $+2$ cations when the anion valence is -2.

The number of solutions for particular pairs of cations, $\omega(A, B)$, decreases with increased valence of either cation for $Z(A) \neq Z(B)$. When $Z(A)$ is already large, increasing $Z(B)$ drastically reduces the number of trial configurations; for example, there is a 20-fold decrease in $\omega(6, B)$ for -1 anions as $Z(B)$ increases from $+1$ to $+6$, and a 10-fold decrease in $\omega(6, B)$ for -2 anions in the same sense. The range of cation coordina-

TABLE III

TRIAL CONFIGURATIONS, $Z(A) = Z(B) = +2$, $\delta_{\max}(X) = 0$

$N_X(A)$	$n(A)$	$N_X(B)$	$n(B)$	$n(X)$
1	3	1	6	2
1	4	1	4	2
2	5	1	10	3
2	6	1	6	3
2	8	1	4	3
2	8	2	8	4
3	8	1	8	4
3	9	1	6	4
3	10	1	5	4
3	10	2	10	5
4	10	1	10	5

Note. $\omega(2, 2) = 11$.

TABLE IV

$\omega(A, B)$ FOR -1 AND -2 (ITALIC) ANIONS SUBJECT TO THE LIMITS IN TABLE II

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
+1	1072	1752	1190	845	627	465
	297	*1004*	*1192*	*1111*	*951*	*833*
+2	(1752)[a]	499	649	431	305	218
		594	*1221*	*1002*	*804*	*657*
+3	(1190)	(649)	189	251	173	127
			475	*755*	*585*	*468*
+4	(845)	(431)	(251)	80	111	78
				251	*415*	*323*
+5	(627)	(305)	(173)	(111)	39	53
					152	*248*
+6	(465)	(218)	(127)	(78)	(53)	20
						93
$\Omega(A)$	5951	3854	2579	1796	1308	961
	5388	*5282*	*4696*	*3857*	*3155*	*2622*

Note. $\Sigma\omega(A, B) = 9174$ and *13,431*.

[a] $\omega(A, B) = \omega(B, A)$; omitted in following tables.

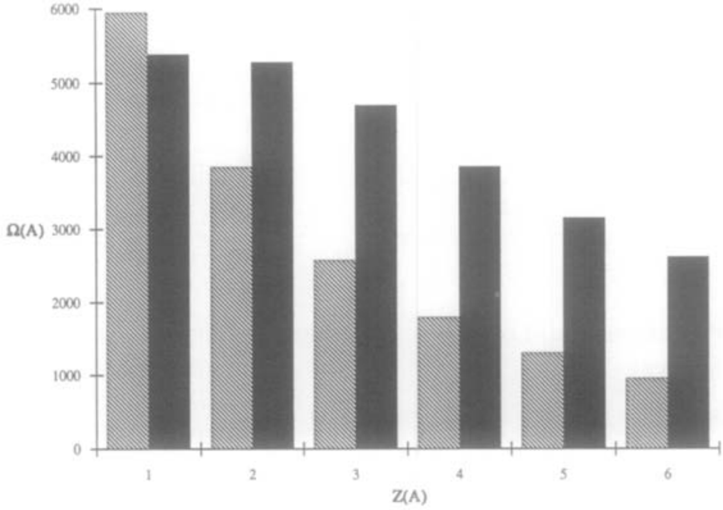

FIG. 1. Histogram of $\Omega(A)$ as a function of $Z(A)$ for arrangements of cations about -1 anions (cross-hatched) and -2 anions (filled) calculated using the limits listed in Table II.

tion numbers—and hence cation bond strengths—is bounded, so the "average" bond strength of a cation increases with its valence. This limits the number of high-valence cations that can be packed around an anion for any range constrained by $\delta_{\max}(Xj)$. This limitation is most pronounced for low-valence anions because high-valence cations typically make substantial contributions to anion site valence.

The number of trial configurations is greatest when $Z(A)$ and $Z(B)$ are equal to or slightly greater than $|Z(X)|$, e.g., $\omega(1, 2)$ for monovalent anions and $\omega(2, 3)$ for divalent anions. A site valence within the range defined by $\delta_{\max}(Xj)$ requires several low-bond-strength cations, but the number of cations is limited by the maximum coordination number of the anion, $n_{\max}(X)$. This combination favors configurations involving cations with valences similar to or somewhat greater than that of the anion.

Table IV illustrates the general consequences of increasing anion valence while all other limits are kept fixed: with the exception of $\omega(1, 1)$ and $\omega(1, 2)$, the number of trial configurations increases with anion valance. The largest percentage increase in $\omega(A, B)$ is for configurations involving at least one high-valence cation; for example, $\omega(1, 2)$ decreases by about 70%, while $\omega(6, 6)$ increases 500%. This is more clearly seen in Fig. 1, a histogram of the total number of trial configurations for a cation of valence $Z(A)$, $\Omega(A)$, plotted as a function of $Z(A)$ for anions of valence -1 and -2. $\Omega(A)$ for -1 anions clearly decrease more rapidly with increasing $Z(A)$ than those for -2 anions. $\Omega(1)$ actually decreases with increased anion valence, meaning this trend is due entirely to an increase in the number of trial configurations involving at least one cation of valence $+2$ or greater. The high site valences of -2 anions permit a larger number of cations of any valence to take part in the site, and thus the number and types of solutions involving high-valence cations increases for any fixed range of anion charge imbalances.

This is of practical importance to $A_aB_bC_cX_X$ crystals in which all anions are bonded to C, as in the CO_3^{2-} anion. The

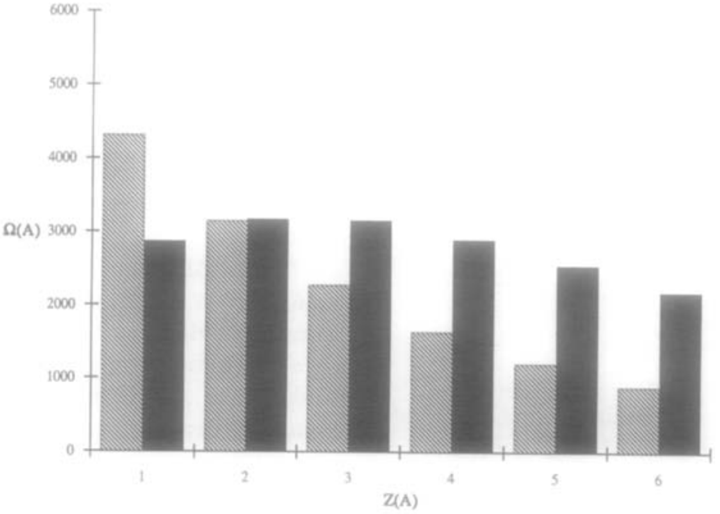

FIG. 2. Histogram of $\Omega(A)$ as a function of $Z(A)$ for arrangements of cations about -1 anions (cross-hatched) and -2 anions (filled) calculated using the limits listed in Table II, save that $n_{\max}(X)$ is reduced from 8 to 6.

actual number of solutions to the Neutral Structure Criterion will be the same whether one treats anion valence as $Z(X)$ or as $Z(X) + \sigma(C)$—in the case of the carbonate anion, for example, whether oxygen is treated as O^{2-} or $(OC_{1/3})^{5/4+}$. At the same time, there are far fewer trial configurations for the reduced effective anion valence *and no other configurations will be valid solutions to the Neutral Structure Criterion.* In summary, the number of trial configurations decreases strongly with cation valence, but increases strongly with anion valence. Reducing anion valence with a "central" cation greatly reduces the number of trial configurations that might satisfy the Neutral Structure Criterion.

VI.A. Decreasing Anion Coordination Number

Table V shows the number of trial configurations, $\omega(A, B)$, for a -1 anion subject to the same limits as those in Table IV save that the maximum coordination number of the anion, $n_{\max}(X)$, is reduced from 8 to 6. This strongly reduces $\omega(A, B)$ for $+1$ and $+2$ cations, but $\omega(A, B)$ for configurations involving $+4$, $+5$, and $+6$ cations are unchanged. Figure 2 compares the number of all solutions for cations of valence $Z(A)$, $\Omega(A)$, for -1 and -2 anions when $n_{\max}(X) = 6$. Increasing anion valence skews the maximum $\Omega(A)$ toward higher values of $Z(A)$, showing that there are few configurations involving one or more high-valence cations in which the coordination number of the anion approaches 6 or more.

The decrease in $\omega(A, B)$ for low-valence

TABLE V

$\omega(A, B)$ FOR -1 ANIONS, $2 \le n(X) \le 6$

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
+1	594	1176	922	697	531	403
+2		422	618	421	302	217
+3			189	251	173	127
+4				80	111	78
+5					39	53
+6						20
$\Omega(A)$	4323	3156	2280	1638	1209	898

Note. $\Sigma\omega(A, B) = 7424$.

TABLE VI

$\omega(A, B)$ FOR -1 ANIONS, $2 \leq n(A), n(B) \leq 9$

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
+1	513	672	403	264	177	120
+2		147	179	111	72	47
+3			51	61	38	25
+4				20	21	14
+5					8	9
+6						3
$\Omega(A)$	2149	1228	757	491	325	218

Note. $\Sigma\omega(A, B) = 2955$.

cations with decreasing $n_{\max}(X)$ results from the elimination of trial configurations involving low-bond-strength cations (i.e., low valence and high coordination number), particularly those in which the anion is overbonded. In a real system, then, $n_{\max}(X)$ imposes a de facto practical limit on $n_{\max}(A)$ or $n_{\max}(B)$ when A or B is a low-valence cation. As anion valence increases the effect of this limit becomes more pronounced: for example, approximately 20% of the original local configurations for -1 anions are eliminated, but approximately 33% of the original configurations for -2 anions are eliminated. In both cases, most configurations lost include at least one $+1$ or $+2$ cation.

VI.B. Decreasing Cation Coordination Number

Table VI shows the number of trial solutions, $\omega(A, B)$, for -1 anions subject to the same limits as those in Table IV, save that the maximum coordination numbers of the cations are reduced from 12 to 9. This drastically decreases $\omega(A, B)$ for any combination of $Z(A)$ and $Z(B)$, reducing the total number of trial configurations from 9174 to 2955. The percentage decrease in configurations involving at least one high-valence cation is disproportionately large; for example, $\omega(1, 1)$ decreases by approximately 50%, but $\omega(6, 6)$ decreases from 20 to 3, or by 85%. Reducing $n_{\max}(A)$ and $n_{\max}(B)$ also strongly affects configurations around -2 anions. This is shown in Fig. 3, where $\Omega(A)$ for -1 and -2 anions are compared. The decrease in the number of trial configurations for -2 anions is less pronounced than for -1 anions because configurations obtained for -2 anions involve fewer low-bond-strength cations. As observed for -1 anions, however, configurations involving high-valence cations are more strongly affected than those involving low-valence cations. In real crystals, cation coordination number tends to decrease with increasing valence and so a more realistic analysis would force maximum cation coordination numbers to decrease with increasing $Z(A)$ and $Z(B)$—this is treated below. We see here that the maximum coordination numbers of cations strongly affect the number of possible arrangements of cations about anion sites in valence crystals, but especially those involving high-valence cations.

VI.C. Limiting Charge-Imbalances on Anions

As might be expected, the number of trial configurations varies directly with the range of charge imbalances permitted on anions, $|\delta_{\max}(Xj)|$. This is illustrated in Fig. 4, a plot of the total number of trial configurations for cations of any valence around -1 and -2 anions as $|\delta_{\max}(Xj)|$ decreases from 0.5 to 0.0 (the curves are spline fits and only approximate interpolations). The total number of trial configurations decreases strongly with $|\delta_{\max}(Xj)|$ and the slope steepens with increasing anion valence. Table VII shows $\omega(A, B)$ for -1 and -2 anions in the extreme limit that $\delta_{\max}(Xj) = 0$, with all other limits as in Table IV. This is a large and important class of valence crystals, so it is encouraging that so few trial configurations remain. When anion site valences exactly compensate anion valences, trial configurations for valence crystals reduce to a small set.

From Table VII one also sees that

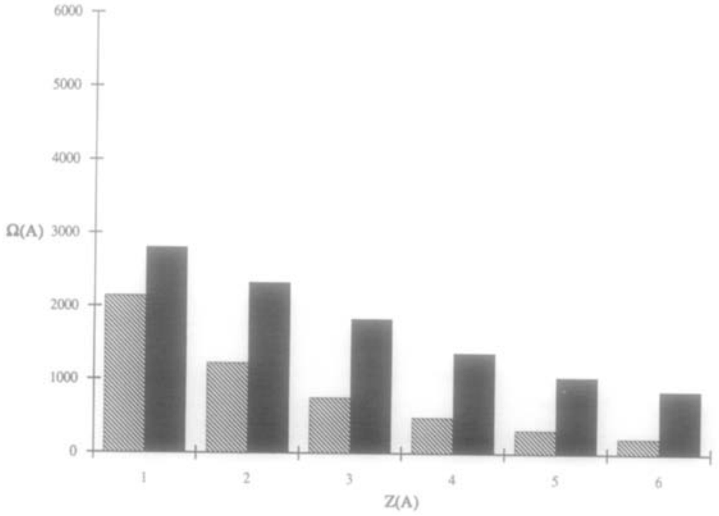

FIG. 3. Histogram of $\Omega(A)$ as a function of $Z(A)$ for arrangements of cations about -1 anions (cross-hatched) and -2 anions (filled) calculated using the limits listed in Table II, save that $n_{\max}(A)$ and $n_{\max}(B)$ are reduced from 12 to 9.

$\omega(A, B)$ do not necessarily follow simple generalizations made above when $\delta_{\max}(Xj) = 0$; for example, in several cases $\omega(5, B)$ are less than $\omega(6, B)$, and the total number of solutions involving $+5$ cations, $\Omega(5)$, is less than $\Omega(6)$. This is an interesting consequence of actual values of bond strength. For the most part all trial configurations involving $+5$ cations require either that $n(A) = n(B)$ or that $n(B)$ is an integral multiple of $n(A)$. Since $n_{\max}(A) = n_{\max}(B) = 12$, this severely restricts the number of trial configurations involving at least one $+5$ cation. Broadly speaking, then, this effect results from the fact that 5 is a prime number. A similar effect results when solutions are examined in terms of the coordination numbers of one or both of the cations—a local minimum in the number of solutions appears at $n(A) = 7$. When one cation has a coordination number of 7 all others must as well if an electroneutral anion site is to be formed.

This points toward a fundamental principle underlying *electroneutral* local configurations: a sum of rational numbers must exactly equal a particular rational number, the real or effective valence of an anion. This is most important in cases when the effective valence of an anion is reduced by a central cation with a fixed coordination number. As an example, the effective valence of oxygen in the carbonate anion is $-\frac{2}{3}$, so carbonates with electroneutral anion sites are generally obtained only when the cation coordination numbers are integral multiples of 3, and individual bond strengths must be no greater than $\frac{2}{3}$. This virtually excludes any possibility of forming a carbonate valence crystal with $+4$, $+5$, or $+6$ cations without placing these cations in sites with extremely high coordination numbers. Similarly, sulfates tend to form electroneutral anion sites with cations whose coordination numbers are integral multiples of 2 because the effective valence of oxygen in the sulfate anion is $-\frac{1}{2}$.

VI.D. Solutions for Underbonded Anions

From above, each overbonded local configuration in a valence crystal has one or more underbonded counterparts, and in this

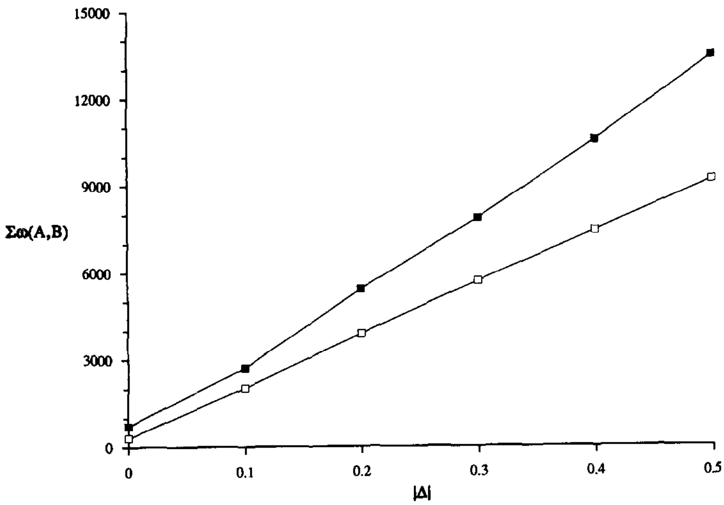

FIG. 4. Variation in the total number of solutions obtained for −1 (open) and −2 anions (filled) subject to the limits listed in Table II, save that $\delta_{max}(X)$ decreases from 0.5 to 0.0.

model the counterpart must be formed by a different configuration of the same cations (or more accurately cation sites) A and B. Because of the initial constraint that the maximum cation coordination number is greater than the maximum anion coordination number, there are more overbonded trial configurations than underbonded and electroneutral trial configurations combined. As a result, many trial configurations for overbonded anion sites have no complementary underbonded counterparts and cannot be used to produce crystals with electroneutral bulk stoichiometries.

Table VIII shows $\omega(A, B)$ for −1 and −2 anions subject to the limits of Table IV save that $-0.5 \leq \delta(X) \leq 0.0$ (thus including electroneutral solutions). Fewer than half of the

TABLE VII

$\omega(A, B)$ FOR −1 AND −2 (ITALIC) ANIONS, $\delta_{max}(X) = 0$

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
+1	42	67	41	28	16	17
	23	*57*	*72*	*49*	*43*	*42*
+2		20	23	14	8	8
		42	*68*	*67*	*33*	*41*
+3			7	9	4	4
			28	*35*	*31*	*23*
+4				3	2	3
				20	*15*	*23*
+5					1	2
					4	*12*
+6						1
						7
$\Omega(A)$	211	140	88	59	33	35
	286	*308*	*257*	*209*	*138*	*148*

Note. $\Sigma\omega(A, B)$ = 320 and *735*.

TABLE VIII

$\omega(A, B)$ FOR −1 AND −2 (ITALIC) ANIONS, $-0.5 \leq \delta(X) \leq 0$

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
+1	699	806	473	308	201	135
	211	*653*	*730*	*605*	*513*	*430*
+2		172	205	127	77	51
		378	*672*	*510*	*385*	*313*
+3			56	67	39	24
			222	*330*	*257*	*197*
+4				20	22	13
				112	*172*	*142*
+5					7	5
					60	*103*
+6						1
						39
$\Omega(A)$	2622	1438	864	557	351	229
	3142	*2911*	*2408*	*1871*	*1490*	*1224*

Note. $\Sigma\omega(A, B)$ = 3508 and *7034*.

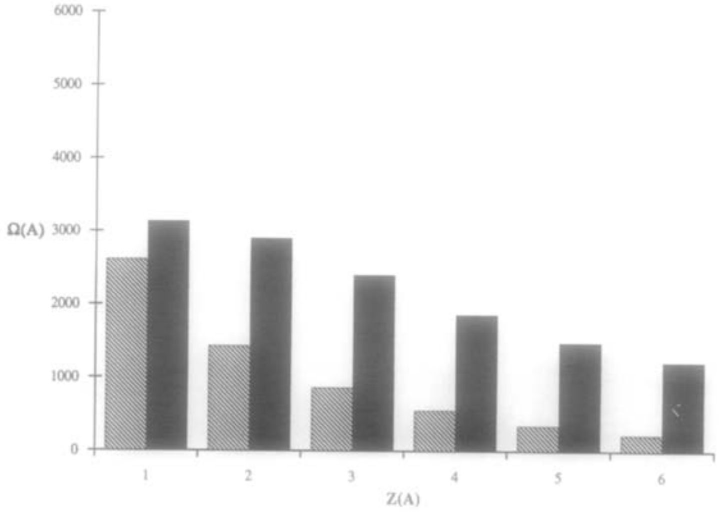

FIG. 5. Histogram of $\Omega(A)$ as a function of $Z(A)$ for arrangements of cations about -1 anions (cross-hatched) and -2 anions (filled) calculated using the limits listed in Table II, save that $-0.5 \leq \delta(X) \leq 0.0$.

initial trial configurations for -1 anions remain. Most strongly affected are combinations involving at least one high-valence cation; for example, $\omega(6, 6)$ decreases from 20 to 1. The total numbers of solutions involving cations of valence $Z(A)$, $\Omega(A)$, around -1 and -2 anions are compared in Fig. 5. Values of $\Omega(A)$ are uniformly greater for -2 anions than for -1 anions. Physically, this suggests that deviations from strict local electroneutrality will be more common in crystals in which $Z(X)$ is relatively large. Conversely, in $A_aB_bC_cX_x$ crystals in which the effective valence of X is reduced by the central cation C one expects local atomic configurations around X to be nearly electroneutral.

VI.E. Realistic Limits on Cation Coordination Numbers

The range of cation coordination numbers considered above is physically unrealistic. We examine the consequences of forcing the maximum coordination number of cations to decrease with increasing cation valence for configurations in which $-0.5 \leq \delta(X) \leq 0.0$ to obtain a somewhat better picture of what combinations of cations can form crystals with electroneutral bulk stoichiometries. The number of underbonded and electroneutral trial configurations, $\omega(A, B)$, for -1 and -2 anions under this limitation is compiled in Table IX (values for the maximum coordination numbers of cations are indicated in the table). The minimum cation coordination number is now 4, but minimum and maximum anion coordination numbers are 2 and 8, as before.

More than 50% of the solutions for -1 anions and more than 70% of the solutions for -2 anions permitted in Table VIII are excluded. As might be expected, configurations involving one or more high-valence cations are most strongly affected. Indeed, solutions involving one or more $+5$ or $+6$ cations are all but eliminated, and the bulk of the configurations referenced in Table IX involve $+1$ or $+2$ cations in combination with cations of other valences. As

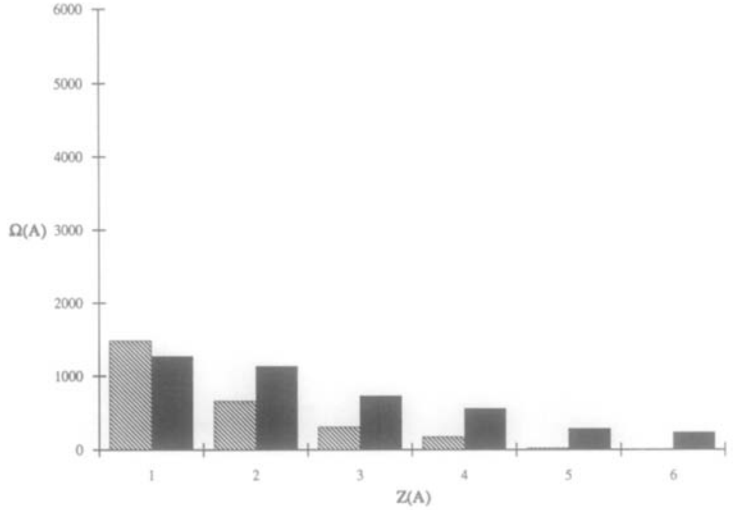

FIG. 6. Histogram of $\Omega(A)$ as a function of $Z(A)$ for arrangements of cations about -1 anions (cross-hatched) and -2 anions (filled) calculated using the limits listed in Table IX.

shown above, more realistic limits on the maximum anion coordination number will eliminate many of the latter as well. If the limit $\delta(X)$ is exactly zero, *most* of these trial configurations are eliminated.

TABLE IX

$\omega(A, B)$ FOR -1 AND -2 (ITALIC) ANIONS, $-0.5\ \delta(X) \leq 0$, VARIABLE $n_{\max}(A, B)$

$Z(B)$	$\omega(1, B)$	$\omega(2, B)$	$\omega(3, B)$	$\omega(4, B)$	$\omega(5, B)$	$\omega(6, B)$
$n_{\max}(A)$	12	10	9	9	7	7
+1	603	495	228	133	25	6
	67	*405*	*296*	*234*	*149*	*127*
+2		72	65	33	4	0
		199	*240*	*172*	*70*	*55*
+3			13	12	0	0
			55	*84*	*34*	*27*
+4				3	0	0
				29	*25*	*20*
+5					0	0
					6	*7*
+6						0
						3
$\Omega(A)$	1490	669	318	181	29	6
	1278	*1141*	*736*	*564*	*291*	*239*

Note. $\Sigma\omega(A, B) = 1692$ and *2304*.

VII. Conclusions

Because the Neutral Structure Criterion is a sum of local atomic configurations, consideration of inherent limits upon local atomic configurations—the minimum and maximum coordination numbers of cations and anions and the magnitude of charge imbalances allowed on anion (or cation) sites—points to restrictions upon the combinations of cations and anions likely to form valence crystals. Analysis of limits for a simple two-cation site model leads to the following generalizations:

(1) The largest number of trial configurations is generated for combinations of cations and anions with valences of similar magnitudes.

(2) Higher anion valences allow more trial configurations for cations with valences similar to, or greater than, those of the anion.

(3) Reduction of an anion's effective valence by a cation of fixed bond strength limits the number of plausible trial configura-

tions to those calculated for the reduced effective valence.

(4) The value of the maximum coordination number of an anion severely limits the number of trial configurations involving at least one low-valence cation, particularly when its valence is less than that of the anion.

(5) The value of the maximum cation coordination number severely limits the number of trial configurations for combinations of cations of any valence, but especially for those including at least one high-valence cation.

(6) The maximum allowed charge imbalance on an anion site severely restricts the number of trial configurations for combinations of cations of any valence, especially for those involving at least one high-valence cation.

(7) When the charge imbalance on an anion site is exactly zero, the number and types of local atomic configurations may be determined largely by the valence and/or coordination numbers of individual cations.

(8) The number of underbonded and electroneutral anion trial configurations permitted by a fixed value $\delta_{\max}(X)$ is smaller than the number of overbonded anion trial configurations.

(9) Realistic limits on the coordination numbers of cations eliminates many trial configurations for any value of $\delta(X)$.

Aside from the numerical results, the most important conclusions from this analysis are: (1) the sum of all cation bond strengths exactly compensates the sum of all anion valences, and the sum of all anion bond strengths exactly compensate the sum of all cation valences; (2) the reference frame of atoms occupying sites and the reference frame of the atoms forming sites are entirely equivalent; and (3) charge imbalances on anion sites must be compensated elsewhere on other anion sites, and likewise for cation sites. When charge imbalances on anion sites are exactly zero, one obtains the electrostatic valence principle of Pauling (*1*), expressed as an equality.

Last, it is interesting that one may describe a set of stoichiometric and structural rules reducing possible local atomic configurations to a finite set: a fixed electroneutral bulk stoichiometry has available to it only a discrete set of possible local atomic configurations. These may be obtained analytically without regard to bond angles, bond lengths, or the exact nature of bonding interactions in valence crystals.

Appendix

Numerical analyses of local anion coordination environments were performed using the program XTAL.PAS. To its favor a well-written Pascal program is largely self-documenting, but to its disfavor there is weak conformance to standards in Pascal compilers. XTAL.PAS is entirely compatible with the ANSI standard except that IEEE floating-point variable type extended was used for certain calculations—this variable type is not available on all Pascal compilers. Copies of the source code are available from AJGE.

The user inputs a single cation valence $Z(A)$, a range of valences for cation B, ranges of cation coordination numbers, a single anion valence (not necessarily an integer), a range of anion coordination numbers, and upper and lower limits for anion charge imbalances. $Z(B)$, $N(A)$, $N(B)$, $n(A)$, and $n(B)$ are stepped between these limits and are used to solve Eq. (19). The value obtained is compared with the range of charge imbalances input by the user. Acceptable answers are written to an ASCII file as $Z(A)$, $Z(B)$, $n(A)$, $n(B)$, $N(A)$, $N(B)$, and the sum of cation bond strengths for each solution (the ASCII files were converted to dBase II file format for analysis).

The limiting parameters give $(12 \ -1)^2$ combinations of cation coordination numbers, C_2^7 or 21 arrangements of cations that do not exceed the limits of 2 and 8 for anion coordination numbers, and six possible valences for B. The program must therefore sort through more than 15,000 possibilities. Most of these are eliminated, however, by using the user-input charge-imbalance limits to set conservative upper and lower bounds for $n(B)$ in the innermost loop. As a result, the program takes only a few seconds to run on an iAP × 86-based computer.

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