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A USEFUL FICTION: POLYHEDRAL MODELING OF MINERAL PROPERTIES

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ABSTRACT. Structures and properties of rock-forming minerals can be modeled by considering cation coordination polyhedra as basic building blocks. The "polyhedral approach" incorporates two assumptions: (1) each type of cation polyhedron has its own characteristic properties (for example, size, shape, thermal expansivity, and fictive thermochemical parameters) which are invariant from structure to structure, and (2) bulk crystal properties can be derived from polyhedral properties if appropriate summation procedures are known. In spite of the fact that both these assumptions are, at best, only first approximations, the polyhedral approach has proven itself to be a valuable method for estimating some hard-to-measure mineral properties. Furthermore, predictions of polyhedral modeling provide a convenient "yardstick" for evaluating observed mineral properties and identifying anomalous data.

I. INTRODUCTION

Most rock-forming minerals are far too complex individually, let alone in multi-species association, to calculate physical properties from existing first principle models. Mineralogists and petrologists have thus resorted to experimental measurements coupled with a variety of simplifying empirical methods in their efforts to describe the structures and properties of natural crystals. Examples of these empirical relations include such well-known trends as "Vegard's Law," which relates molar volume to ionic radius (Vegard and Dale, 1928); the rule of Gladstone and Dale (1864) as applied by Larsen and Berman (1934), who predicted mean refractive index from weight percentage of oxides; and Birch's Law (Birch, 1960; 1961), which correlates mineral density and mean atomic weight with compressional wave velocity. Empirical relationships of this kind are usually introduced as useful tools in the prediction of properties that may be difficult to obtain experimentally or theoretically. Birch's Law and related models, for example, have proven especially valuable in constraining compositional models of the Earth's mantle. Of equal importance, however, are the insights that empirical relationships can provide on the origin of mineral structures and properties. In this regard, empirical relationships should be viewed as valuable "yardsticks" against which the behavior of minerals may be compared, rather than rigid "laws" to which minerals are expected to conform. The success of an empirical model, therefore, lies as much in its ability to identify interesting anomalies, as in its success in predicting mineral structures or properties.

Pauling's Rules and the Significance of the Polyhedron

Perhaps the best known empirical approach to modeling the complexities of mineral structures is that of Pauling (1929; 1960), who systematized aspects of mineral-like structures in a set of "rules" under the heading, "The principles determining the structure of complex ionic crystals." Pauling's first rule states the importance of cation coordination polyhedra, which are formed by anions about each cation in the structure; cation-anion distance is equal to the sum of ionic radii, and coordination number is often related to the radius ratio. This first rule is a recasting of Goldschmidt's rule that the number of anions surrounding a cation tends to be as large as possible. The second rule is a statement of ionic charge balance; the sum of valency bonds (cation charge divided by coordination number) to each anion is approximately equal to the valence of that anion. Pauling's third and fourth rules state that polyhedra of small, highly-charged cations (such as Si^{4+}) tend not to share edges or faces; these polyhedra will usually lie as far apart as possible. Finally, the fifth rule simplifies the structural analysis of chemically complex phases by noting that "the number of essentially different kinds of constituents in a crystal tends to be small." In summary, Pauling's rules systematize the nature of nearest-neighbor interactions in mineral structures. These principles thus have been instrumental in the solution of many complex crystal structures.

Pauling's presentation and much of the subsequent development of his ideas are couched in the terminology of an ionic model. Cations and anions, formal charge, and electrostatic forces are integral to the development. Several authors have noted, however, that even materials that are quite covalent obey rules "isomorphous to those applying in ionic crystals" (Burdett and McLarnan, 1984; see also Bent, 1968). It would be a mistake, therefore, to apply Pauling's methodology exclusively to ionic crystals, just as it would be erroneous to cite conformity with these rules as evidence for some degree of ionic character.

Pauling's rules are an explicit statement of the importance of nearest-neighbor bonding in determining the structure of mineral-like compounds. It is interesting to note that Pauling's description focuses on the role of cation coordination polyhedra rather than on clusters of cations about anions. While the second rule relating to charge balance applies equally well to positive or negative ions, it is the cations coordinated to regular anion clusters that differ little from mineral structure to structure. Anion coordination groups, on the other hand, show much greater variation in different crystal structures.

There are at least two reasons for this lack of uniformity in anion clusters. First, oxygen is the only important anion in most rock-forming minerals, whereas there are several important cations. Cations are surrounded uniformly by oxygens in most minerals, whereas anions have several different cation nearest neighbors. This situation might well be reversed in a world of one dominant cation (magnesium) and

several common anions (equal amounts of coexisting oxygen, sulfur, selenium, fluorine, chlorine, and bromine). Our focus on cation polyhedra, therefore, may be largely an artifact of the mineralogical data base. Second, cations tend to demonstrate a much wider range of valence. Cations of valence one through five are common in minerals, whereas anions of valence one or two predominate. One might, therefore, expect more uniformity in the anion arrays than the cation arrays in most crystal structures. In developing empirical models of mineral structures and properties, it is logical to concentrate on those aspects of atomic arrangements—cation coordination polyhedra—that recur often.

Molecular Mimicry in Minerals

Pauling's rules, which are based on the observed structures of crystals, first elucidated the significance of cation coordination polyhedra. Some of the most compelling evidence in support of polyhedral modeling, however, has come from studies of isolated molecules. A variety of investigations, both experimental and theoretical, have shown that small one- or two-polyhedral clusters of oxygen surrounding silicon, boron, magnesium, or other cation are almost identical topologically to those units in mineral structures. This phenomenon, termed "molecular mimicry" by Gibbs and coworkers (Zhang and others, 1985; Gibbs and Boisen, 1986; Gibbs, Finger, and Boisen, 1987), is demonstrated by the conformation of such silicate-related molecules as H_4SiO_4—monosilicic acid and $H_6Si_2O_7$—disilicic acid (Newton, O'Keeffe, and Gibbs, 1980). These molecules display bond distances and angles almost identical to those in silicate minerals (O'Keeffe, Domenges, and Gibbs, 1985).

Molecular mimicry has proven especially important in the application of *ab initio* molecular orbital calculations to minerals. Most molecular orbital computations have been limited by computer speed and memory to problems of no more than about 200 basis functions (generally fewer than a dozen nonhydrogen atoms). Early efforts to model silicates or borates were by necessity restricted to even smaller clusters. These studies were often criticized on the basis of an assumed dissimilarity of isolated molecules, such as $H_6Si_2O_7$, compared to crystalline solids with continuous, periodic linkages of atoms. Nevertheless, as molecular orbital studies on minerals have increased in number and sophistication, it has become evident that the conformational details of polyhedral molecules generated by *ab initio* molecular orbital procedures are remarkably faithful to crystalline subunits.

The successes of molecular orbital modelling are many. The bond distances, coordination numbers, and bond length-bond strength systematics of cation-anion clusters have been reproduced (Gibbs, Finger, and Boisen, 1987). The sympathetic variation of bond length with T-O-T bond angle in tetrahedral framework structures has been modeled (Geisinger, Gibbs, and Navrotsky, 1985). And, perhaps most significantly, electron density distributions virtually identical to those determined experimentally have been calculated for portions of silicate

structures (Gibbs and Boisen, 1986). One important conclusion of these and other molecular orbital calculations is that polyhedral electron densities—and by implication polyhedral configuration and properties—are relatively independent of long-range polyhedral interactions, at least as long as approximate local charge balance is maintained.

The Polyhedral Approach

The polyhedral approach is a logical extension of Pauling's rules and the observations of molecular mimicry. The objective is to model various physical properties of crystals on the basis of observed or assumed properties of constituent cation coordination polyhedra. The two fundamental assumptions of this "polyhedral approach" are:

1. Each different type of cation coordination polyhedron (SiO_4 tetrahedron or MgO_6 octahedron) has properties that are invariant from structure to structure. These properties may be directly measurable (polyhedral volume or compressibility) or they may be fictive (polyhedral heat capacity or elastic modulii); and,
2. Properties of minerals may be derived from polyhedral properties if appropriate summation procedures can be identified.

The most obvious flaw in this polyhedral modeling scheme is the total neglect of crystal energy contributions by second-nearest neighbor cation-cation interactions (O'Keeffe and Hyde, 1981) and all longer-range interactions. The "properties" of each type of polyhedron are modeled as constants from structure to structure, regardless of the ways in which they are interconnected. Many attributes of crystals—including all anisotropic characteristics—cannot be derived from the polyhedral approach without resorting to the additional information of the type and orientation of polyhedral linkages. Considerable effort in polyhedral modeling, therefore, has been directed toward quantifying polyhedral linkage schemes and their relationship to structure.

The polyhedral approach has proven useful in predicting structural details, physical properties, and phase stability of minerals, in spite of the fact that both of its two assumptions are, at best, only first approximations and in some instances are demonstrably false. The objective of this paper is to review recent experimental and theoretical results that reveal some of the useful applications, as well as the significant limitations, of the polyhedral approach. Parts II and III review the geometrical characteristics of polyhedra and their linkages, respectively. Part IV delineates polyhedral properties, both observed and fictive, and their use in modeling crystals.

II. POLYHEDRAL PARAMETERS AND THEIR VARIATIONS

Polyhedral Parameters

Composition and formal charge.—Cation coordination polyhedra are described by several parameters: the cation species and its formal charge, the anion species and its formal charge, the coordination

number, and the geometrical form. In many compounds these parameters are unambiguous. In MgO, for example, the Mg^{2+} cation is surrounded by six O^{2-} anions in a regular octahedron, denoted $^{VI}Mg^{2+}$. Similarly, in forsterite, Mg_2SiO_4 the structure consists of two nonequivalent $^{VI}Mg^{2+}$ cations and silicon in tetrahedral coordination ($^{IV}Si^{4+}$). Most fully-ordered, stoichiometric oxides and silicates conform to this ideal situation.

In compounds with more complex chemistry, in particular when cation nonstoichiometry or disorder occurs, the polyhedral parameters are taken as the average over the entire crystal for each nonequivalent polyhedron. Consider the example of a disordered intermediate plagioclase with composition (NaCa) $(Al_3Si_5)O_{16}$. The average cation species of the large alkali site is $(Na_{0.5}Ca_{0.5})$ with a formal charge of 1.5; that of the tetrahedral sites is $(Al_{0.375}Si_{0.625})$ with a formal charge of 3.625. In partially ordered intermediate plagioclase the description of average polyhedral parameters for each nonequivalent polyhedron becomes much more complicated: Cation occupancy information for each crystallographically distinct polyhedron is required.

The anion species is O^{2-} in all examples considered in this paper; extension of the polyhedral approach to halides is straightforward, but consideration of sulfides, nitrides, and other compounds with predominantly covalent bonding is not generally possible unless clearly identifiable polyhedral clusters are present. Thus, the approach works for PbS in the galena (rock salt) structure but is not easily applied to FeS_2 in the pyrite structure, which does not have a simple polyhedral topology.

Coordination number.—The concept of cation coordination number, defined as the number of anions associated with a given cation, predates Pauling by more than a decade (Pfeiffer, 1916). In most stoichiometric oxides and silicates the coordination number is an integer that is obvious by inspection. The exact coordination number of large cation sites, however, especially those with more than 6 coordinating anions, may be ambiguous. The difficulty of assigning an integral coordination number is evident by considering continuous changes that some structures undergo with varying temperature, pressure, or composition. Interlayer alkali cations of micas are associated with 12 oxygen anions, which in most species separate into 6 shorter ("inner") or 6 longer ("outer") bond distances. The difference between these two sets of alkali-oxygen distances is often referred to as the interlayer site Δ. In many micas, such as taeniolite ($KLiMg_2Si_4O_{10}F_2$; Toraya and others, 1977) and annite (approx $KFe_3AlSi_3O_{10}(OH)_2$; Hazen and Burnham, 1973), the inner and outer distances are nearly equal, so Δ is zero, and interlayer coordination is 12. In other micas, however, Δ may be as large as 1.0 Å. In synthetic $KMg_3AlGe_3O_{10}F_2$ (Toraya and others, 1978), for example, the 6 shorter K-O distances are 2.8 Å while the 6 longer K-O distances are 3.6 Å; potassium in this mica might justifiably be assigned a coordination number of 6. Continuous changes in mica composition,

temperature, or pressure lead to continuous variations in Δ. For example, a decrease in the size of the alkali site relative to the other mica layers (either by substitution of Na for K, or by an increase in pressure, or by a decrease in temperature), will result in an increase in Δ. Since all values of Δ from 0.0 to about 1.0 are possible, it follows that all values of coordination number from 12 to 6 are also possible; there exists no straightforward method to calculate the coordination number (integral or otherwise) of the alkali cation polyhedron. A somewhat arbitrary expression such as:

$$p = 6[1 + (1 - \Delta)^{0.5}] \quad (1)$$

might be applied to indicate a relative scale of coordination number, p, for the micas, but this relation is not general. Similar ambiguities in coordination number occur in the alkali feldspars (Prewitt, Sueno, and Papike, 1976), in sodium zirconium silico-phosphates ($Na_{1+x}Zr_2(Si_xP_{3-x})O_{12}$; Hong, 1976), noncubic perovskites such as sodium niobate ($NaNbO_3$; Megaw, 1974), and many other compounds with large, irregular alkali or alkaline earth sites of variable composition and noncubic symmetry.

There have been several attempts to quantify "effective coordination number" in a more rigorous way. Brunner and Schwarzenbach (1971) defined an effective coordination number, *KZ* (for koordinationzahl), on the basis of histograms of distances from a central atom to surrounding atoms. In most structures a "gap" in this histogram divides coordinating atoms from noncoordinating atoms. Hoppe (1979) devised a more complex, though somewhat *ad hoc,* procedure for calculating effective coordination number, ECoN, on the basis of deviations of observed cation-anion and anion-anion bond distances from values expected from the ionic radii of Shannon (1976). Brown and Shannon (1973), alternatively, assigned varying bond strengths to different cation-anion pairs on the basis of the bond lengths. Each of these approaches recognizes the nonideal nature of cation coordination clusters that occur in many compounds.

Polyhedral volume.—Polyhedral volume is defined as the space enclosed by constructing planes through each set of three adjacent coordinating anions about a given cation. The only required data are the unit-cell parameters and the atomic coordinates of the anions. A computer program to calculate polyhedral volumes has been described by Swanson and Peterson (1980), and a complete listing of program VOLCAL by L. W. Finger to calculate polyhedral volumes and distortion indices is provided by Hazen and Finger (1982, app. 3). Typical polyhedral volumes for common cation-anion clusters are 2.2 $Å^3$ for SiO_4 tetrahedra, 9 $Å^3$ for AlO_6 octahedra, and 12.5 $Å^3$ for MgO_6 octahedra. The largest cation coordination polyhedra in common rock-forming minerals are the alkali positions in feldspars and feldspathoids, with volumes in excess of 20 $Å^3$.

Polyhedral distortions.—An ideal, or "regular," cation polyhedron is defined as a cluster with all anion-anion edges of equal length, and all adjacent anion-cation-anion angles equal. Examples of regular cation polyhedra in crystals are the LiO_4 tetrahedron in the antifluorite-type Li_2O, the MgO_6 octahedron in NaCl-type MgO, the $CsCl_8$ cube in CsCl, and the CaO_{12} dodecahedron in cubic perovskite-type $CaTiO_3$. Ideal planar cation "polyhedra," such as the CO_3 groups of carbonate or square-planar groups in some platinum and iron compounds, are also conveniently included in this group. All these atom clusters are characterized by just one cation-anion distance and one anion-cation-anion angle for adjacent anions.

Most cation polyhedra deviate slightly from shape ideality, and considerable effort has been devoted to the quantification of these distortions. Quadratic elongation and bond angle variance (Robinson, Gibbs, and Ribbe, 1971) are two commonly cited distortion parameters. Quadratic elongation, $\langle\gamma\rangle$, is defined as:

$$\langle\gamma\rangle = \Sigma\,[(l_i/l_0)^2/n] \tag{2}$$

where l_0 is the center-to-vertex distance of a regular polyhedron of the same volume, n is the coordination number of the central atom, and l_i is the distance from the central atom to the ith coordinating atom. A regular polyhedron has a quadratic elongation of 1, whereas distorted polyhedra have values greater than 1. Bond angle variance, σ^2, is defined as:

$$\sigma^2 = \Sigma\,[(\theta_i - \theta_0)^2/(n - 1)] \tag{3}$$

where θ_0 is the ideal bond angle for a regular polyhedron (for example, 90° for an octahedron or 109.47° for a tetrahedron), n is the coordination number, and θ_i is the ith adjacent bond angle from outer, to central, to outer atoms. Angle variance is zero for a regular polyhedron and positive for a distorted polyhedron. Robinson, Gibbs, and Ribbe (1971) noted a good correlation exists between quadratic elongation and bond angle variance, and Fleet (1976) demonstrated that this correlation is exact for several types of symmetric polyhedral distortions.

Dollase (1974) presented an alternative procedure for quantifying polyhedral distortions. His method is based on a comparison of the distorted polyhedron with a reference polyhedron of similar volume. The reference polyhedron may be regular, or it may possess lower symmetry (for example, a trigonally-distorted octahedron). The distortion parameter is a single number that represents the mean deviation of observed and reference polyhedral anion positions. The Dollase approach is particularly useful in quantifying polyhedral deviations from a particular symmetry, or in identifying similarities among like polyhedra in different structures.

On the Variability of Polyhedral Geometry

In reviewing polyhedral parameters it is useful to consider the range of size, shape, and distortion of some common polyhedra. Silicate tetrahedra display little variation from structure to structure. Average silicon-oxygen distance ranges from about 1.61 Å in framework silicates to 1.65 Å in orthosilicates, with corresponding polyhedral volumes of about 2.10 to 2.25 $Å^3$. Oxygen-silicon-oxygen intratetrahedral angles rarely deviate by more than 10° from the ideal 109.47° value. The longest and shortest oxygen-oxygen edges of a SiO_4 tetrahedron typically differ by no more than 0.15 Å or about ±5 percent from the 2.7 Å average value.

Aluminum octahedra are more variable in geometry than silicon tetrahedra, with average Al-O distances ranging from less than 1.9 Å to almost 2.0 Å, corresponding to octahedral volumes from 8.8 to 9.6 $Å^3$. Intraoctahedral O-Al-O angles may deviate by as much as 15° from the ideal 90° value. Longest and shortest O-O edges differ by up to 0.3 Å or about ±10 percent from the 2.7 Å average.

Octahedra of divalent magnesium are significantly more variable in geometry than those of trivalent aluminum (fig. 1). Average Mg-O distances range from 2.05 to 2.15 Å corresponding to polyhedral volumes of about 12 to 13 $Å^3$. Oxygen-magnesium-oxygen bond angles sometimes deviate by more than 20° from the regular octahedral value of 90°. Distorted octahedra with O-O edges that differ by up to 0.4 Å (about ±15 percent) from the 2.9 Å average are well known in minerals.

The BeO_4 tetrahedra, like MgO_6 octahedra, are much more variable than tri- and tetravalent cation polyhedra (fig. 2). Average tetrahedral Be-O distances are near 1.65 Å, but tetrahedral volumes range from 2.0 to 2.3 $Å^3$. In most BeO_4 tetrahedra the O–Be–O angles are within a few degrees of the ideal 109.47°, but in beryl these angles range from 91° to 131°.

Oxygen-oxygen edge lengths in beryl, similarly, show a large variation from 2.3 to 3.0 Å, compared to an average 2.7 Å value.

In summary, polyhedra of a given type may display significant variations in polyhedral geometry from structure to structure. Variations of ±2 percent in average bond distance, ±4 percent in polyhedral volume, and ±15 percent in O-O edge lengths are typical of divalent polyhedra in common minerals. In general, cations with greater cation valence display less variation from structure to structure. Nevertheless, it is evident that the first assumption of the polyhedral approach—that of invariance of such polyhedral properties as size and shape—is at best only a first-order approximation.

III. POLYHEDRAL LINKAGES

A mineral structure may be characterized by the types of its coordination polyhedra and the manner in which those polyhedra are

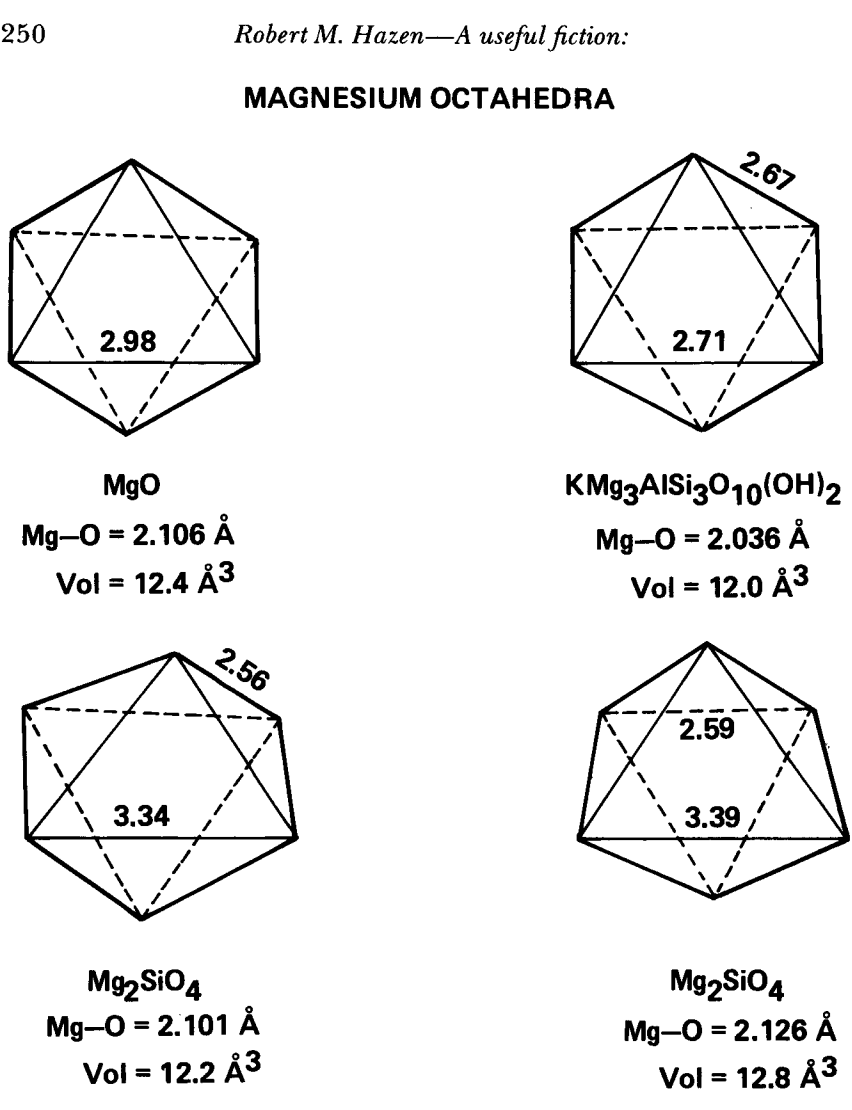

Fig. 1. The variability of MgO_6 octahedra in oxides and silicates.

linked together. Two polyhedra may be joined by a shared face (three or more common anions), a shared edge (two common anions), a shared corner (one common anion), or by intermolecular forces (no shared elements). For the purposes of polyhedral modeling, it is necessary to identify the types and distribution of polyhedral linkages throughout a structure; therefore, a classification of mineral structures on the basis of polyhedral linkages is now being developed. A complete description of this classification scheme is beyond the scope of the present review, but a

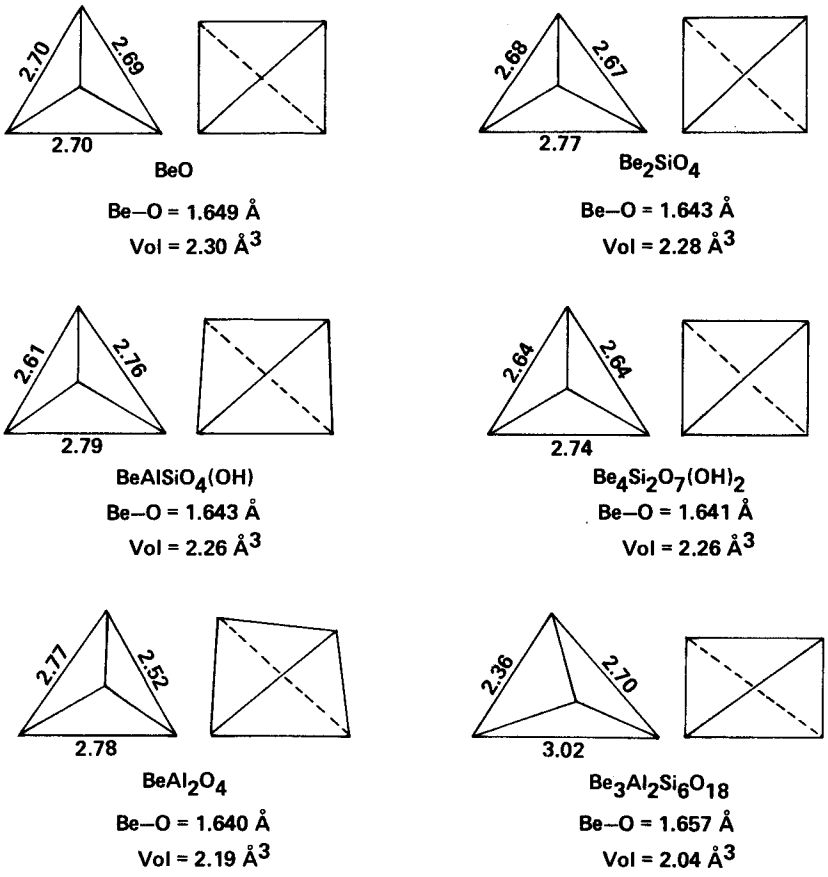

Fig. 2. The variability of BeO_4 tetrahedra.

brief summary will elucidate the rationale and applications of the approach.

The basis of the classification is the distribution of rigid versus deformable polyhedral linkages in the structure. In this context a rigid linkage is defined as a cluster of atoms that tends to undergo little deformation with changes in temperature, pressure, or composition of adjacent polyhedra. Thus, the shared face between AlO_6 octahedra in corundum is called a rigid polyhedral linkage because the three oxygens that define the shared face retain their relative positions. The shared corner between two SiO_4 tetrahedra in α-quartz, on the other hand, is considered to be a very deformable linkage, because the three atoms that define the Si–O–Si angle undergo significant variations in relative positions with changes in temperature and pressure. The rationale for

classifying minerals on the basis of these rigid versus compliant linkages is that many physical properties, and in particular the anisotropy of these properties, are directly related to the rigidity of linkages. Of particular interest in the earth sciences are the close correlations between polyhedral linkage rigidity and mineral elasticity, thermal expansivity, and thermochemical systematics. These relations are examined in more detail in section IV below.

The three most rigid polyhedral configurations are: (1) shared faces between two polyhedra in which the valences of the two cations sum to +3 or more, (2) shared edges between two polyhedra with the valences of the two cations summing to +4 or more, and (3) rings of corner-sharing polyhedra with cation-anion-cation angles that are restricted. The relative rigidity of shared faces and edges is qualitatively proportional to the sum of the valences of the two cations; thus the Al^{3+}-Al^{3+} shared faces in corundum (sum +6) are more rigid than Mg^{2+}-Mg^{2+} shared faces in pyrope (sum +4). Similarly, the Si^{4+}-Mg^{2+} shared edges in forsterite are more rigid than the Mg^{2+}-Mg^{2+} shared edges in the same structure. Restricted angles may arise from 3-member rings of corner-linked polyhedra, as observed in bertrandite, bromellite, and phenakite (Be-Be-Be or Be-Be-Si tetrahedral rings, with T-O-T angles constrained to be close to 120°). Alternatively, in some high-symmetry compounds certain angles are fixed. This behavior is exemplified by the 6-fold symmetry of the 6-member Si_6O_{18} rings of beryl and high-cordierite (Si-O-Si angles constrained to about 168°). All other types of polyhedral linkages are more flexible. Shared edges or faces between alkali cations, for example, are much more deformable than those between 2^+ or 3^+ cation polyhedra. Corner-linked polyhedra, in the absence of other restrictions, are more flexible than polyhedra that share edges or faces. And, of course, intermolecular bonds are many times weaker than cation-anion interactions.

It is particularly instructive to visualize mineral structures by considering the three-dimensional distribution of points, segments, triangles, or rings that represent shared corners, shared edges, shared faces, or restricted rings. Many common rock-forming minerals are characterized by continuous three-dimensional patterns of shared faces, shared edges, or rigid cation-anion-cation angles. Rock salt, garnet, scheelite, and spinel are examples of structure types with this rigid linkage of polyhedral elements. Corner-linked structures of high symmetry such as β-quartz, β-cristobalite, and cubic perovskites are also characterized by such a rigid three-dimensional network of linkages, because of constraints on cation–anion–cation angles. In contrast, flexible framework structures, including α-quartz, alkali feldspars, low-symmetry alkali perovskites, and low-symmetry zeolites, have no rigid interpolyhedral links. Angles between polyhedra vary significantly with changes in temperature, pressure, or alkali composition. Most crustal minerals are intermediate in character, with some rigid and some flexible linkages. In alkali micas, for example, octahedral edge-sharing

leads to a continuous rigid network within each octahedral layer, in contrast to the more flexible linkages in the alkali and silicon tetrahedral layers.

This view of crystals—in terms of the rigidity of their shared polyhedral elements—reveals a significant fact: The anisotropic behavior of chain, sheet, or framework silicates may be considered to be a consequence of the distribution of rigid shared edges and faces between polyhedra *adjacent* to tetrahedral chains, layers, and so on, rather than the arrangement of the silicon tetrahedra themselves. Indeed, the distribution of edge- and face-sharing octahedra is the basis for at least one magnetic classification system of minerals (Coey and Ghose, 1986). As the close relationships between polyhedral properties and mineral behavior are explored it will be necessary to keep these distinctive patterns of polyhedral linkages in mind.

IV. POLYHEDRAL PROPERTIES AND MINERAL BEHAVIOR

Pressure-Temperature-Volume Equations of State

Polyhedral equations of state.—Perhaps the most intensively studied polyhedral property has been the variation of polyhedral volume with temperature and pressure. The volume of a cation polyhedron may be derived from crystal structure data; therefore, high-pressure and high-temperature crystal structure studies contain information on the pressure-temperature-volume (*P–T–V*) equations-of-state of each constituent polyhedron.

An important conclusion of these nonambient crystallographic studies is that thermal expansion and compressibility are independent of structure for many types of cation polyhedra. In the case of MgO_6 octahedron compressibility, for example, polyhedra in periclase, diopside, enstatite, forsterite, monticellite, and phlogopite all have volume compressibilities of about 0.67 ± 0.03 $Mbar^{-1}$ (fig. 3). Similarly, BeO_4 tetrahedra in bertrandite, beryl, bromellite, chrysoberyl, euclase, and phenakite all have volume compressibilities consistent with 0.47 $Mbar^{-1}$ (Hazen and Au, 1985, 1986). The volume thermal expansion of MgO_6 octahedra (Hazen and Finger, 1982; fig. 6-4) is approx $4.0 \pm 0.4 \times 10^{-5}$ $°C^{-1}$ between 0° and 1000° C for each of seven different oxides and silicates. The similarity of thermal expansion behavior of different beryllium tetrahedra is particularly striking (fig. 4). Tetrahedra in beryl, bromellite, chrysoberyl, and phenakite (with two nonequivalent tetrahedra) all have the same slope *and* curvature. An average expansion coefficient of about $2.5 \pm 0.3 \times 10^{-5}$ C^{-1} is observed between 0° and 1000°C. It is possible, therefore, to assign a single coefficient of thermal expansion and compressibility to each of these cation polyhedra. The first assumption of the polyhedral approach—that of the constancy of polyhedral properties—appears to obtain for many cations.

Two simple empirical equations relate these observed constant coefficients of polyhedral thermal expansion and compressibility to

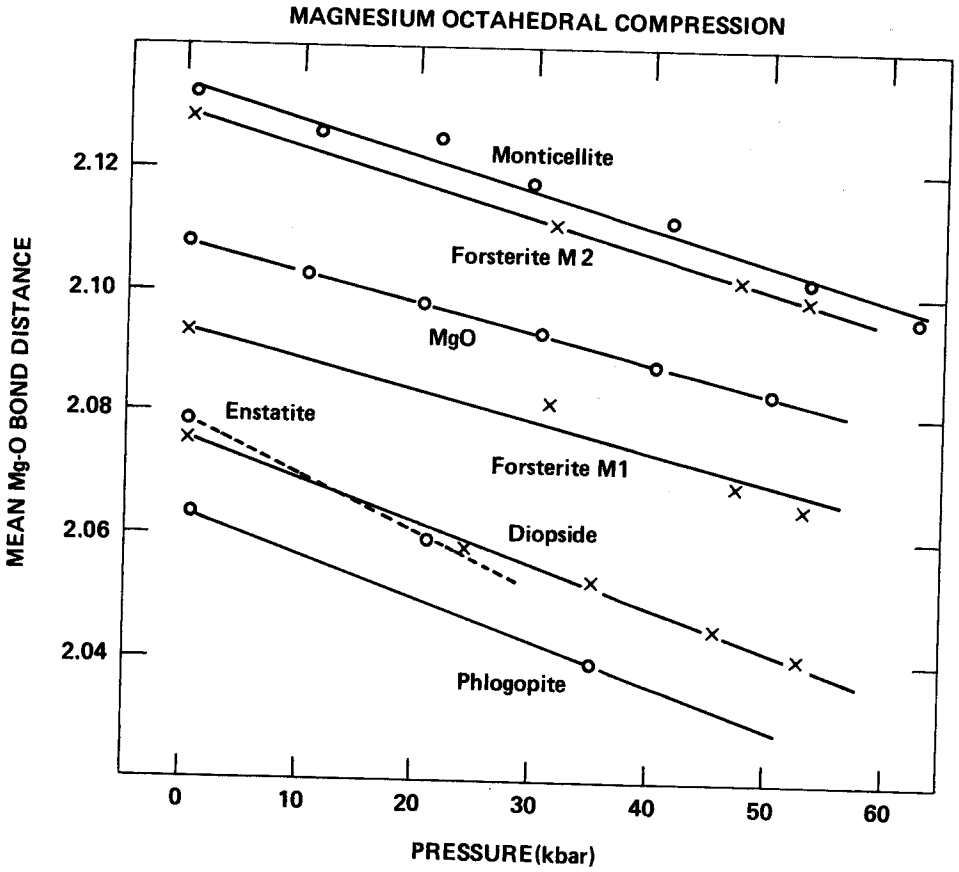

Fig. 3. Average Mg-O bond distances (Å) in magnesium-oxygen octahedra versus pressure (kb) for monticellite (Sharp, Hazen, and Finger, 1987), forsterite (Kudoh and Takeuchi, 1985), diopside (Levien, Prewitt, and Weidner, 1980), enstatite (Ralph and Ghose, 1980), phlogopite (Hazen and Finger, 1978a), and MgO.

polyhedral bonding parameters (Hazen and Finger, 1982). Polyhedral thermal expansion is inversely proportional to Pauling bond strength:

$$\text{Polyhedral } \alpha_{1000} \approx 1.25 \pm 0.12\ (n/z) \times 10^{-5}\ ^\circ C^{-1}, \qquad (4)$$

where α_{1000} is the average polyhedral volume expansion between 25° and 1000°C, n is the cation coordination number, and z is the cation valence. Polyhedral volume compressibility, β, is proportional to average cation-anion distance cubed, d^3, and inversely proportional to cation valence, z:

$$\text{Polyhedral } \beta \approx 0.133 \pm 0.015\ (d^3/z)\ \text{Mbar}^{-1}, \qquad (5)$$

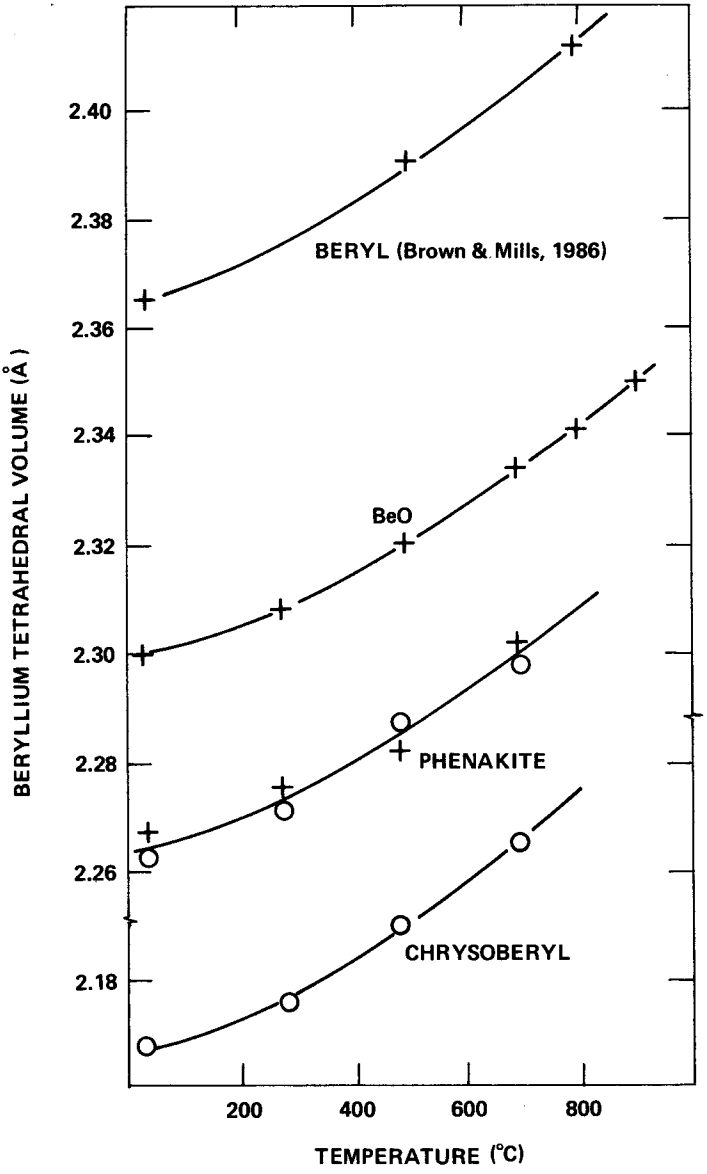

Fig. 4. Average BeO_4 tetrahedral volume ($Å^3$) versus temperature (°C) for beryl (Brown and Mills, 1986), BeO (Hazen and Finger, 1986), and phenakite and chrysoberyl (Hazen and Finger, 1987).

These two simple empirical relations are sufficient to predict polyhedral volumes as a function of temperature and pressure in most minerals. In a slight modification, these equations (4) and (5) have been extended to include polyhedra in halides, sulfides, and other materials (Hazen and Finger, 1982).

It is instructive to review the two types of polyhedra that deviate most from eq (5). Eight-coordinated polyhedra in the cesium chloride type structure are much less compressible than predicted. The cesium chloride structure is unique among the many structures examined in that all polyhedra (simple cubes) share all faces with adjacent polyhedra. As a consequence, second-nearest neighbor cation-cation distances in CsCl-type compounds are just 15 percent longer than the cation-anion distances. Strong second-nearest neighbor interactions appear to cause the relative incompressibility of these compounds. Conversely, the great majority of compounds that conform to the empirical polyhedral compressibility relation appear to be little affected by such second-nearest neighbor effects.

On the other hand, several types of cation-oxygen polyhedra tend to be significantly more compressible than predicted by eq (5). Tetrahedral Zn in ZnO, tetrahedral Si in many silicates, and octahedral V in V_2O_3, for example, are all 50 percent more compressible than expected. Zn-O and Si-O bonds are often described as "more covalent" than divalent and alkali cation-oxygen bonds, whereas V_2O_3 is an unusual oxide with metallic luster and conductivity. Thus, positive deviations from the empirical trend of eq (5) may be related to some aspect of bond character.

Important objections to the concept of invariant polyhedral thermal expansion and compressibility have been voiced by Liebermann (personal commun.). He argues that a given type of polyhedron in different structures may experience different *effective* local pressures as a result of pressure shielding or intensification by surrounding polyhedral units. This situation certainly occurs, for example, in the case of cubic $Pm3m$ perovskites such as high-temperature KWO_3, $NaWO_3$, and $NaNbO_3$, in which the rigid framework of tungsten or niobium octahedra precludes significant compression or expansion of the alkali 12-coordinated polyhedron. Similar situations obtain in high-symmetry forms of cordierite, zeolites, eucryptite, and other minerals with rigid corner-linked frameworks of relatively incompressible polyhedra which define cavities containing large interstitial cation. The concepts of polyhedral thermal expansion and compressibility are thus called into question for these special types of structures. However, thermal expansion and compressibility data for the great majority of alkali and divalent cation polyhedra are relatively constant for a variety of structures and thus do not necessarily support Liebermann's view.

In the case of SiO_4 tetrahedra, however, there is mounting evidence for significant variation in compressibility in different structures. The empirical expression of Hazen and Finger (1982) predicts a

silicon tetrahedral compressibility of about 0.15 $Mbar^{-1}$, a value that does conform to the least compressible silicon tetrahedra measured thus far. However, a considerable range of tetrahedral compressibilities have been reported, from about 0.15 $Mbar^{-1}$ in quartz (Levien, Prewitt, and Weidner, 1980) to approx 0.25 $Mbar^{-1}$ in diopside (Levien and Prewitt, 1981) to more than 0.50 $Mbar^{-1}$ in forsterite (Kudoh and Takeuchi, 1985). A general trend seems to be emerging; tetrahedra in frameworks with flexible T–O–T angles are less compressible than tetrahedra in flexible chains, which appear, on average, to be less compressible than isolated tetrahedra. It is possible that these trends are related to the systematic variation of Si-O distances versus T–O–T angle documented by Gibbs and coworkers (Gibbs, 1982; Geisinger, Gibbs, and Navrotsky, 1985) and may bear a close relationship to the "effective local pressure" proposed by Liebermann. Liebermann's hypothesis may thus have validity and should be the subject of further systematic study.

Mineral equations of state.—A knowledge of polyhedral equations of state is necessary, but not sufficient, to derive mineral equations of state. There are not, as yet, any simple procedures to predict mineral thermal expansion or compressibility from those of the constituent polyhedra. It is possible, however, to classify expansion and compression behavior on the basis of the polyhedral linkage systematics described in section III.

Hazen and Finger (1985) identified three mechanisms by which crystals expand or compress with changing temperature or pressure: variations in polyhedral volume, bending of interpolyhedral angles, and changes in intermolecular separations. Another possible compression mechanism—that of polyhedral distortion without appreciable cation-anion distance changes (in other words changes in anion–cation–anion bond angles)—does not appear to be a significant factor in the thermal expansion or compression of minerals.

Intermolecular distances increase and decrease at least an order of magnitude more than cation-anion bonds. In any molecular compound, including such layer minerals as graphite and talc as well as virtually all organic crystals, intermolecular changes dominate the *P–T–V* systematics of the crystal. Expansion or compression parallel to those bonds, furthermore, is always many times greater than in planes with no intermolecular bonding. Thus, layered compounds with intermolecular bonding have one highly variable unit-cell length, whereas crystals of chain-like molecules have two such directions.

Flexible cation-anion-cation angles, which are commonly associated with shared polyhedral corners, also lead to large thermal expansion and compressibility in crystals. Large volume changes of α-quartz with temperature and pressure are almost entirely the result of T-O-T bending (Levien, Prewitt, and Weidner, 1980), and the maximum expansion or compression direction in minerals such as alkali feldspars (Prewitt, Lueno, and Papike, 1976) and bertrandite (Hazen and Au, 1986) are approximately parallel to T–O–T angles that undergo significant changes. Thus, in structures with intermolecular

bonds or flexible interpolyhedral angles, it is possible to predict compression anisotropies. However, the magnitudes of axial expansion or compression resulting from these mechanisms have yet to be quantified in any useful predictive scheme.

In many minerals bond expansion and compression, alone, control the *P–T–V* equation of state. In most simple binary compounds, including those with the rock salt, fluorite, cesium chloride, wurzite, sphalerite, corundum, β-quartz, α-rhenium oxide, β-cristobalite, high-tridymite, and rutile structures, the polyhedral equations of state are identical to those of the crystal (Hazen and Finger, 1982). This correspondence results from the constraints on polyhedral orientations in these structures: macroscopic volume changes can only result from changes in polyhedral volume. In minerals with the olivine, spinel, scheelite, and other structures with no interpolyhedral flexibility a similar situation obtains. Expansion and compression of these minerals are equal or only slightly less than those of the most deformable (in these cases usually a 2+ or 3+ cation) polyhedron. Feldspars, garnets, and noncubic perovskites, similarly, display thermal expansion and compression close to those of the large alkali or divalent cation polyhedra; in these minerals the corner-linked frameworks of octahedra and/or tetrahedra deform to the size of the large polyhedra. A similar behavior is expected for most feldspathoids and zeolites. It appears possible, therefore, to predict the magnitudes of thermal expansion and compression for many minerals on the basis of the known equations of state for constituent polyhedra.

Fictive Thermochemical Properties of Polyhedra

The Robinson and Haas procedure.—Mineralogists have long recognized that heat capacities and calorimetric entropies can be estimated by summation of the heat capacities of constituent oxides or elements (Kopp, 1864). Robinson and Haas (1983) elaborated on this method by considering fictive heat capacities of polyhedral components rather than oxides. Experimental heat capacity data between 0° and 1200°C for 61 minerals were analyzed by weighted, simultaneous, multiple least-squares techniques. For each of 17 types of cation polyhedra as well as fluorine, hydroxyl, and H_2O, Robinson and Haas derived a fictive polyhedral heat capacity of the form:

$$C'_p = a + 2bT + c/T^2 + f\,T^2 + g/T^{1/2}, \quad (6)$$

where C'_p is the fictive heat capacity, T is the absolute temperature, and *a* through *g* are coefficients derived from the least-squares analysis. For most polyhedra *a*, *b*, and *g* are the only nonzero coefficients. Thus, for example, fictive heat capacity of a SiO_4 tetrahedron is:

$$C'_p = 109.38 - 0.005552T - 1083.5/T^{1/2}. \quad (7)$$

Robinson and Haas also presented values for fictive polyhedral calorimetric entropy, which is closely related in form to the heat

capacity expression:

$$S' = a\ln T + 2bT - c/T^2 + e + f\,T^2/2 - 2g/T^{1/2} \qquad (8)$$

Mineral heat capacities and calorimetric entropies are calculated from fictive polyhedral values by a simple linear summation over all polyhedra in one formula unit. The Robinson and Haas calculated heat capacities generally agree with experimental values to better than ±2 percent over the temperature range 0° and 1200°C. This accuracy is a significant improvement over the ±5 percent errors typical of the oxide summation procedure. It is evident, therefore, that the heat capacity of minerals is sensitive to the coordination environment of cations as well as the type of cation. A similar conclusion was demonstrated by Jeanloz (1982) in his examination of the variation of thermodynamic properties across phase transitions involving changes in cation coordination.

It is instructive to examine the 61 minerals cited by Robinson and Haas (1983) in more detail to identify phases that deviate most significantly from the predicted heat capacities. This information is not included in their publication, but the authors have kindly loaned their computer output for this analysis. Predicted heat capacities for biopyriboles (pyroxenes, amphiboles, and micas) conform extremely well with observed values. Average differences between observed and calculated heat capacities for such minerals as diopside, tremolite, muscovite, and phlogopite are smaller than ±1 percent over most of the temperature range 0° to 1200°C where experimental values are available. Similar close agreement is found for most feldspars, feldspathoids, and many orthosilicates.

The least satisfactory agreement is obtained for olivines (forsterite, fayalite, and Ca-olivine), β-quartz, and β-cristobalite. Each of these phases has a calculated heat capacity that is too large—by as much as 2 to 5 percent. These olivines and high-symmetry silica polymorphs share one significant structural feature, namely that *all* changes in volume with temperature must result from changes in cation-anion bond lengths. No changes in interpolyhedral angles are possible because of the inflexibility of polyhedral linkages. This behavior is distinct from that of biopyriboles, feldspars, feldspathoids, garnets, aluminosilicates, and many other minerals in which some interpolyhedral angle variations accompany thermal expansion.

The calculated heat capacity of α-quartz is significantly less than the observed values; this mineral is the worst such case. Low quartz is unusual in that virtually all its thermal expansion results from changing Si–O–Si angles; all interpolyhedral linkages are flexible. It seems likely, therefore, that whole-polyhedron vibrations, which are possible adjacent to a flexible shared corner, may be a significant aspect of mineral heat capacity that is not explicitly treated in the Robinson and Haas polyhedral approach. Biopyriboles and other minerals with a few flexible corner-shared polyhedra are fit well by the fictive polyhedral parameters. But extreme cases, such as α-quartz with all flexible linkages

or olivine with no flexible linkages, tend to have observed heat capacities higher or lower, respectively, than calculated.

It may at first seem paradoxical that feldspars and feldspathoids, which like α-quartz are known to have a high percentage of flexible interpolyhedral linkages, show close agreement between observed and calculated heat capacities. It should be noted, however, that these are the only minerals included in the Robinson and Haas calculations that contain significant proportions of alkali cations in "6-coordination." (Micas, for example, were assigned alkalis in "8-coordination.") The fictive polyhedral parameters for "6-coordinated" alkali sites thus probably have the effects of interpolyhedral vibrations imbedded in their coefficients as a consequence of the least-squares fitting of polyhedral coefficients.

This analysis suggests that an improved empirical summation procedure might be developed by the inclusion of a simple polyhedral linkage coefficient that represents the number or flexibility of corner-shared structural elements.

Fictive heat capacity of the BeO_4 tetrahedron.—Recently-determined high-temperature heat capacities of minerals in the system BeO–Al_2O_3–SiO_2–H_2O (BASH) by Hemingway and others (1986) provide a test of the Robinson and Haas model. New data for hydrous and anhydrous beryl ($Be_3Al_2Si_6O_{18} \pm H_2O$), phenakite ($Be_2SiO_4$), euclase ($BeAlSiO_4(OH)$), bertrandite ($Be_4Si_2O_7(OH)_2$), and chrysoberyl ($BeAl_2O_4$) have been incorporated into the Robinson and Haas data base. Fictive heat capacities of tetrahedral silicon, octahedral aluminum, hydroxyl, and H_2O were constrained to be the same as those in Robinson and Haas (1983, table 3). Only the *a*, *b*, and *g* coefficients of tetrahedral beryllium were refined. The resulting fictive polyhedral heat capacity for tetrahedral Be is:

$$C'_p = 98.194 - 0.009277T - 1217.1/T^{1/2}. \quad (9)$$

Calculated heat capacities of hydrous and anhydrous beryl, euclase, chrysoberyl, and phenakite all agree within about 1 percent of the observed values throughout the observed range 25° to 525°C, whereas the calculated heat capacities of bertrandite are systematically too large by about 2 percent (figs. 5 and 6). The agreement between observed and calculated heat capacities is thus comparable to experimental error of the calorimetric measurements, themselves.

In the case of mineral heat capacities, therefore, the two assumptions of the polyhedral approach appear to obtain to at least a first approximation. There exist fictive polyhedral properties that are invariant from structure to structure, and mineral heat capacities can be calculated by a simple linear summation of these polyhedral values. It is important to note, however, that the fictive polyhedral heat capacities and calorimetric entropies calculated by the Robinson and Haas procedure, while closely related to the energetics of nearest-neighbor cation-anion bonding, are not exclusively the result of these interactions. The

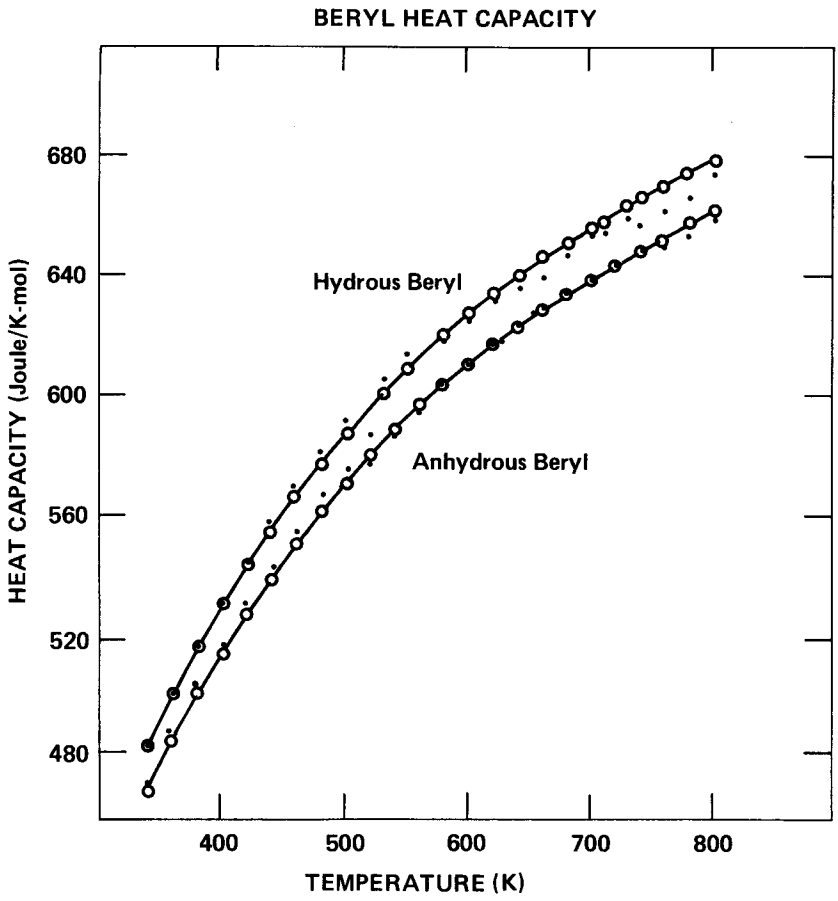

Fig. 5. Calculated (circles) versus observed (dots) heat capacities of hydrous and anhydrous beryl versus temperature (K).

least-squares procedure used to derive the polyhedral properties tends to average out energy associated with inter-polyhedral effects amongst the several constituent polyhedra of each mineral.

Polyhedral Elastic Constants and Mineral Elasticity

Polyhedral elastic constants.—Perhaps the most ambitious application of the polyhedral approach has been the attempt to identify polyhedral elastic constants and to use these constants in a rigid-ion model for the prediction of crystal elasticity (Au, 1984; Au and Hazen, 1985; Au and Weidner, 1986). One rationale for adopting this approach is that conventional central-force models are unable to account for observed Cauchy violations (cubic $c_{44} \neq c_{12}$) that are observed in most oxides and silicates. The many-body interactions inherent in polyhedral

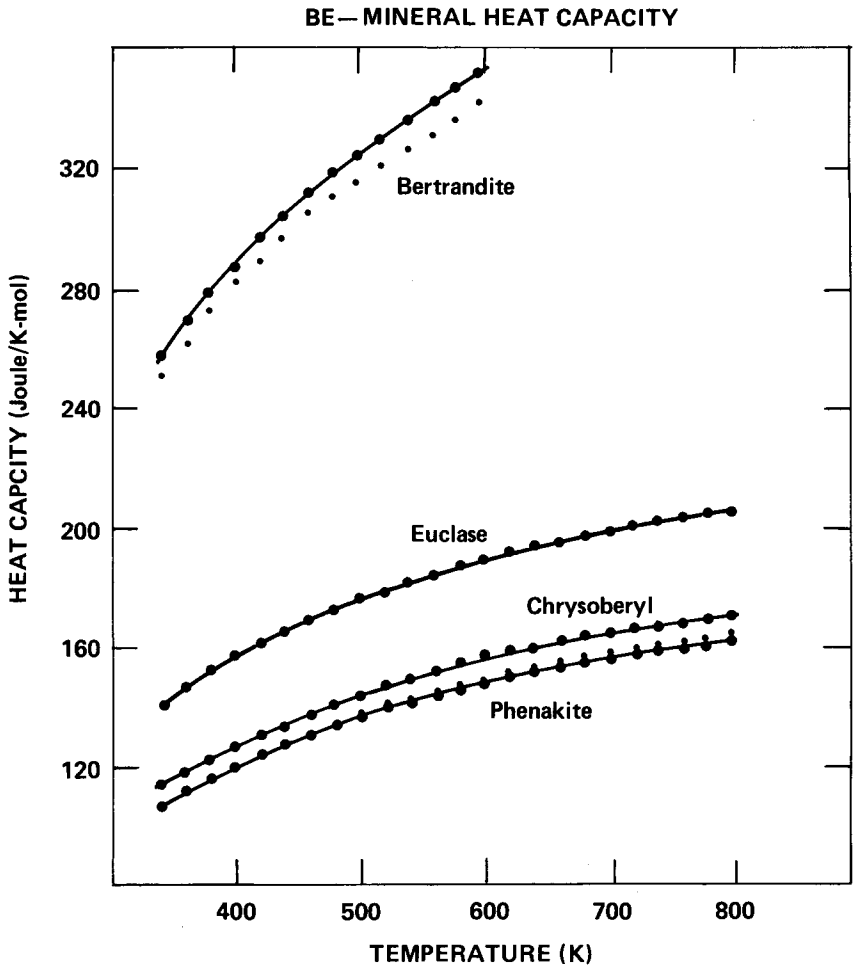

Fig. 6. Calculated (circles) versus observed (dots) heat capacities of bertrandite, euclase, chrysoberyl, and phenakite.

modeling incorporate noncentral forces and thus may provide a simple scheme for predicting real crystal moduli.

Polyhedral elastic moduli (c_{11}, c_{44}, and c_{12}) for magnesium, cobalt, nickel, manganese, and aluminum octahedra were derived from the single-crystal moduli of MgO, CoO, NiO, MnO, and Al_2O_3, respectively. Au then used these polyhedral parameters to model minerals with the olivine structure: forsterite, Co_2SiO_4, Ni_2SiO_4, Mn_2SiO_4, and chrysoberyl. In addition to three constrained octahedral cation elastic constants, the model includes three variable tetrahedral cation elastic moduli, four variable anharmonic interatomic spring coefficients, and a variable

ionicity factor. Elastic constants of forsterite were reproduced to within an average of 3 percent (Au and Weidner, 1986) and those of chrysoberyl to within 1 percent (Au and Hazen, 1985). In spite of this apparent success, however, there remain significant difficulties with the procedure. In the case of forsterite, 8 variables (the 3 tetrahedral moduli, 4 spring coefficients, and ionicity) were optimized in an effort to match the 11 observed forsterite elastic constants. The eight coefficients were varied to match the known forsterite elastic moduli, rather than to predict elasticity from first principles. No obvious physical significance can be ascribed to the eight variables, and, what is particularly disturbing, the interatomic spring constants and fictive silicon tetrahedral elastic moduli are *not* transferable to the other silicate olivines.

The case of chrysoberyl is also unconvincing: The three aluminum octahedral elastic moduli were treated as variables, so 11 variables were used to model the 11 crystal elastic constants. The parameterization led to excellent agreement between observed and fitted elastic moduli, as expected in a case where the number of variables equals the number of fitted parameters. Unfortunately, the aluminum octahedral elastic constants calculated for chrysoberyl do not agree with those derived from the oxide, corundum. In addition, the anharmonic spring coefficients for O-O, Al-Al, and Al-0 in corundum versus chrysoberyl are calculated to have very different values—different signs in the cases of O-O and Al-O. It is not clear, therefore, whether this polyhedral approach can provide significant insight or predictive capability.

Polyhedral linkages and mineral elasticity.—In spite of the questionable success of quantitative polyhedral modeling of elastic constants, it is certain that a knowledge of polyhedral compressibilities and linkage rigidity is central to a qualitative understanding of mineral elasticity. Elastic properties of numerous minerals, including beryl (Yoon and Newnham, 1973), pyroxenes (Weidner, Wang, and Ito, 1978; Levien, Prewitt, and Weidner, 1980; Bass and Weidner, 1984), garnets (Leitner, Weidner, and Liebermann, 1980), aluminosilicates (Vaughan and Weidner, 1978), and micas (Vaughan and Guggenheim, 1986), have been rationalized on the basis of the types and linkages of polyhedra. In muscovite mica (Vaughan and Guggenheim, 1986), for example, compression within the atomic layers is equal to that of the aluminum octahedra, which comprise the least compressible polyhedral layers. Compression perpendicular to the layers is much greater, because the relatively soft potassium polyhedra are free to compress in that direction. Thus, $c_{11} \approx c_{22} \gg c_{33}$ in muscovite and other micas. By the same token, shear within the plane of mica layers is constrained by the edge-sharing octahedral array, but shear perpendicular to layers is much easier because of the deformable alkali polyhedra; thus, $c_{66} \gg c_{55} \approx c_{44}$.

Mineral elasticity is controlled by the distribution of rigid versus weak structural elements. Rigid elements include shared polyhedral faces and edges and inflexible cation–anion–cation angles. Weak elements include large 1^+ or 2^+ cation polyhedra, flexible interpolyhedral

angles, and intermolecular bonds. Any crystal direction with continuous rigid linkages, such as the chain direction in pyroxenes or any direction within a mica layer, will have a relatively small compressibility, approximately equal to the polyhedral compressibility of the rigidly-linked units that lie in that direction. Any crystal plane with continuous rigid linkages will have relatively large shear modulus. Conversely, any crystal plane with continuous array of flexible linkages or deformable polyhedra will display relatively large compressibility perpendicular to that layer and relatively small shear moduli in any plane perpendicular to the layer.

Other Polyhedral Properties

Characteristic vibrational frequencies.—A number of physical characteristics of condensed matter, in addition to equation of state, thermochemical parameters, and elasticity, may be related to the constituent polyhedra. Each type of polyhedron, for example, has characteristic vibration frequencies (internal vibration modes) that can be used to identify cation species in fluids and glasses (Mysen, Virgo, and Seifert, 1985) as well as to assign bands in vibrational spectra of minerals (McMillan, 1985). Kieffer (1979) made use of the characteristic frequencies of silicon tetrahedra in her formulation relating silicate mineral heat capacities to vibrational spectra. Such polyhedra as WO_4 and MoO_4 tetrahedra are also characterized by a remarkable constancy of internal mode vibrational frequencies.

Melt properties.—The polyhedral approach would seem to be particularly well suited for the estimation of silicate melt properties. Procedures to predict silicate liquid properties such as density (Bottinga and Weill, 1970) and viscosity (Bottinga and Weill, 1972) from oxide summations have proven useful in modeling geological systems. Such models would be physically more plausible and probably more accurate if recast in a polyhedra context.

Each type of polyhedron acts as a network former or network modifier in a manner that, on average, affects the density and viscosity of the liquid. If appropriate polyhedral coefficients for density and viscosity were known, then melt properties could be predicted from a knowledge of melt structure and composition. Furthermore, it might be possible to constrain models of melt structure if composition and physical properties were known.

Polyhedral stability fields.—Given the relative invariance of polyhedral properties from structure to structure, it is intriguing to speculate on the possibility of polyhedral stability limits—conditions of temperature and pressure beyond which a given cation-coordination cluster is energetically unfavorable compared to other clusters. Hazen and Finger (1978b), for example, noted that virtually all silicate minerals have 4-coordinated silicon at surface conditions, but all known silicates above 300 kb have 6-coordinated silicon. Furthermore, the estimated average Si-O bond distance for silicon tetrahedra in structures at their

pressures of transformation are often approx 1.59 Å. Does this value represent an energetic limit for silicon tetrahedra? Do other polyhedra have similar limits?

In the case of MgO_6 octahedra in silicates a transformation to 8-coordinated magnesium is observed in several minerals at pressures where average Mg-O distance approaches about 2.05 Å. This distance cannot be considered a polyhedral limit, however, because MgO in the rock salt structure persists to pressures well above 1 Mbar, at which pressure the Mg-O distance is about 1.9 Å (Mao and Bell, 1979). Similarly, several silicates with calcium in octahedral coordination transform when the average Ca-O distance is compressed to about 2.35 Å, but CaO with octahedral calcium is stable at high pressures where the Ca-O bond is much shorter (Sharp, Hazen, and Finger, 1987). Thus, while polyhedral stability limits may obtain at extremely high temperatures or pressures, it is evident that they will not be of much use in constraining models of hypothetical mineral structures at extreme conditions.

V. SUMMARY

The polyhedral approach may be summarized by considering its successes and its shortcomings. The advantages of the polyhedral approach include the following:

1. The approach has led to the recognition of certain polyhedral properties, notably thermal expansion and compression, that are remarkably constant from structure to structure for many types of polyhedra.

2. The method has a proven potential for predicting mineral heat capacities and holds promise for predicting thermal expansion and compression of minerals. The polyhedral approach also provides a sound qualitative framework for understanding mineral elasticity.

3. The polyhedral approach reveals interesting anomalies (the compressibility of CsCl, for example) that shed light on relationships among structure, bonding, and properties.

4. Empirical relations developed by polyhedral modeling provide constraints on theoretical models of mineral behavior. The relation between polyhedral compressibility and d^3/z (eq 5), for example, may provide a key to realistic pair potentials in oxides and silicates.

Polyhedral modeling of minerals is limited because of the following factors:

1. The assumption of invariant polyhedral properties is, at best, only a first approximation. In several notable cases—the compression of silicon tetrahedra, for example—significant variations occur from structure to structure.

2. The assumption that summation procedures can be found to relate polyhedral properties to bulk crystal properties is questionable, *unless* polyhedral linkages can be included in the formalism. The important, and sometimes dominant, effects of polyhedral linkage

(particularly linkage rigidity) are not yet sufficiently well quantified to calculate most mineral properties from polyhedral properties.

3. No allowance is made for significant differences in polyhedral distortions from structure to structure. The energies associated with crystal field effects, Jahn-Teller distortions, or lone pairs are not considered.

4. Any disordering of polyhedra is treated as ideal; excess properties of mixing are not predicted.

5. The method works only for polyhedral compounds; several classes of materials, including metals and alloys, organic and organometallic crystals, and many "covalent" sulfides and sulfosalts, are not composed of obvious polyhedral units.

One of the legacies that Dave Wones left his students was the importance of viewing rocks in a variety of ways. Rocks may be treated as assemblages of minerals, each with its characteristic structure and properties. They may be quantified as weight percentages of oxide components or as ratios of normative minerals. They may be considered graphically in terms of fictive chemical components in multi-dimensional space, or they may be described mechanically as three-dimensional networks of crystalline interfaces, with little regard for chemical or mineralogical details. Geophysical models of rocks may emphasize the elastic, electrical, or magnetic behavior of the bulk material, whereas geochemical models often detail isotopic and trace element distributions among adjacent mineral grains. Each of these different descriptive approaches provides insight on a rock's present state and geological history; a comprehensive rock description might include aspects of all these approaches.

The polyhedral approach provides yet another, complementary way to describe a rock. Each cation in a rock system is likely to reside in a favored polyhedral environment. Those polyhedra, and the linkage patterns that they adopt, form the condensed phases of virtually all common crustal materials. A recognition of polyhedral properties, and an understanding of how those properties are reflected in mineral behavior, can provide insight into the physics and chemistry of earth materials.

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References

Au, A. Y., ms, 1984, Theoretical modelling of the elastic properties of mantle silicates: Ph.D. Thesis, State Univ. New York at Stony Brook.

Au, A. Y., and Hazen, R. M., 1985, Polyhedral modeling of the elastic properties of corundum (α-Al_2O_3) and chrysoberyl (Al_2BeO_4): Geophys. Research Letters, v. 12, p. 725–728.

Au, A. Y., and Weidner, D. J., 1986, Theoretical modelling of the elastic properties of forsterite: a polyhedral approach: Phys. Chem. Minerals., in press.

Bass, J. D., and Weidner, D. J., 1984, Elasticity of single-crystal orthoferrosilite: Jour. Geophys. Research, v. 89, p. 4359–4371.

Bent, H. A., 1968, Tangent-sphere models of molecules: VI: Ion-packing models of covalent compounds: Jour. Chemical Ed., v. 45, p. 768–778.

Birch, F., 1960, The velocity of compressional waves in rocks, 1.:Jour. Geophys. Research, v. 65, p. 1083–1102.

———— 1961, The velocity of compressional waves in rocks, 2.: Jour. Geophys. Research, v. 66, p. 2199–2224.

Bottinga, Y., and Weill, D. F., 1970, Densities of liquid silicate systems calculated from partial molar volumes of oxide components: Am. Jour. Sci., v. 269, p. 169–182.

———— 1972, The viscosity of magmatic silicate liquids: a model for calculation: Am. Jour. Sci., v. 272, p. 438–475.

Brown, G. E., Jr., and Mills, B. A., 1986, High-temperature structure and crystal chemistry of hydrous alkali-rich beryl from the Harding pegmatite, Taos County, New Mexico: Am. Mineralogist, v. 71, p. 547–556.

Brown, I. D., and Shannon, R. D., 1973, Empirical bond-strength-bond-length curves for oxides: Acta Cryst., v. A23, p. 266–282.

Brunner, G. O., and Schwarzenbach, D., 1971, Zur Abgrenzung der Koordinationssphare und Ermittlung der Koordinationszahl in Kristallstrukturen: Zeitschr Krist., v. 133, p. 127–133.

Burdett, J. K., and McLarnan, T. J., 1984, An orbital interpretation of Pauling's rules: Am. Mineralogist, v. 69, p. 601–621.

Coey, J. M. D., and Ghose, S., 1986, Magnetic phase transitions in silicate minerals: Internat. Mineralog. Assoc. Gen. Mtg., 14th, Stanford Univ., Stanford, Calif. Abs. with Programs, p. 79.

Dollase, W. A., 1974, A method of determining the distortion of coordination polyhedra: Acta Cryst., v. A30, p. 513–517.

Fleet, M. E., 1976, Distortion parameters for coordination polyhedra: Mineralog. Mag., v. 40, p. 531–533.

Geisinger, K. L., Gibbs, G. V., and Navrotsky, A., 1985, A molecular orbital study of bond length and angle variations in framework silicates: Physics Chemistry Minerals, v. 11, p. 266–283.

Gibbs, G. V., 1982, Molecules as models for bonding in silicates: Am. Mineralogist, v. 67, p. 421–450.

Gibbs, G. V., and Boisen, M. B., Jr., 1986, Molecular mimicry of structure and electron density distributions in minerals: Materials Research Sci., in press.

Gibbs, G. V., Finger, L. W., and Boisen, M. B., Jr., 1987, Molecular mimicry of the bond length-bond strength variations in oxide crystals: Physics Chemistry Minerals, v. 14, p. 327–331.

Gladstone, J. H., and Dale, T. P., 1864, Researches on the refraction, dispersion, and sensitiveness of liquids: Royal Soc. London Trans., v. 153, p. 337–348.

Hazen, R. M., and Au, A. Y., 1985, High-pressure crystal structures and polyhedral bulk moduli of minerals in the system BeO-Al_2O_3-SiO_2: Am. Geophys. Union Trans., v. 66, p. 357.

Hazen, R. M., and Au, A. Y., 1986, High-pressure crystal chemistry of phenakite (Be_2SiO_4) and bertrandite ($Be_4Si_2O_7(OH)_2$): Physics Chemistry Minerals, v. 13, p. 69–78.

Hazen, R.M., and Burnham, C.W., 1973, The crystal structures of one-layer phologopite and annite: Am. Mineralogist, v.58, p. 889–900.

Hazen, R. M., and Finger, L. W., 1978a, The crystal structures and compressibilities of layer minerals at high pressure. II. phlogopite and chlorite: Am. Mineralogist, v. 63, p. 293–296.
———— 1978b, Crystal chemistry of silicon-oxygen bonds at high pressure: implications for the earth's mantle mineralogy: Science, v. 201, p. 1122–1123.
———— 1982, Comparative Crystal Chemistry: New York, John Wiley & Sons, 231 p.
———— 1985, Crystal compression: Scientific American, v. 252, p. 110–117.
———— 1986, High-pressure and high-temperature crystal chemistry of beryllium oxide: Jour. Appl. Physics, v. 59, p. 3728–3733.
———— 1987, High-temperature crystal chemistry of phenakite Be_2SiO_4 and chrysoberyl $BeAl_2O_4$: Physics Chemistry Minerals, v. 14, p. 426–434.
Hazen, R. M., and Wones, D. R., 1972, The effect of cation substitutions on the physical properties of trioctahedral micas: Am. Mineralogist, v. 57, p. 103–129.
Hemingway, B. S., Barton, M. D., Robie, R. A., and Haselton, H. T., Jr., 1986, Heat capacities and thermodynamic functions for beryl, $Be_3Al_2Si_6O_{18}$, phenakite, Be_2SiO_4, euclase, $BeAlSiO_4(OH)$, betrandite, $Be_4Si_2O_7(OH)_2$, and chrysoberyl, $BeAl_2O_4$: Am. Mineralogist, v. 71, p. 557–568.
Hong, H. Y.-P., 1976, Crystal structures and crystal chemistry in the system $Na_{1x}Zr_2Si_xP_{3-x}O_{12}$: Materials Research Bull., v. 11, p. 173–182.
Hoppe, R., 1979, Effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR): Zeitschr. Krist., v. 150, p. 23–52.
Jeanloz, R., 1982, Effect of coordination change on thermodynamic properties, in Akemoto, S., and Manghnani, M. H., eds., High Pressure Research in Geophysics: Boston, D. Reidel, 479–498.
Kieffer, S. W., 1979, Thermodynamics and lattice vibrations of minerals. II. Vibrational characteristics of silicates: Rev. Geophysics Space Physics, v. 17, p. 20–34.
Kopp, H., 1864, Ueber die specifische warme der starren korper: Ann. der Chemie und Pharmacie, Suppl. 3, p. 289–342.
Kudoh, Y., and Takeuchi, Y., 1985, The crystal structure of forsterite Mg_2SiO_4 under high pressure up to 149 kbar: Zeitschr. Krist., v. 171, p. 291–302.
Larsen, E. S., and Berman, H., 1934, The microscopic determination of the nonopaque minerals: U.S. Geol. Survey Bull., v. 848, 266 p.
Leitner, B. J., Weidner, D. J., and Leibermann, R. C., 1980, Elasticity of single crystal pyrope and implications for garnet solid solution series: Phys. Earth Planetary Interiors, v. 22, p. 111–121.
Levien, L., and Prewitt, C. T., 1981, High-pressure structural study of diopside: Am. Mineralogist, v. 66, p. 315–323.
Levien, L., Prewitt, C. T., and Weidner, D. J., 1980, Single-crystal x-ray study of quartz at pressure: Am. Mineralogist, v. 65, p. 920–930.
Levien, L., Weidner, D. J., and Prewitt, C. T., 1981, Elasticity of diopside: Physics Chemistry Minerals, v. 4, p. 105–113.
Mao, H. K., and Bell, P. M., 1979, Equations of state of MgO and ϵ-Fe under static pressure conditions: Jour. Geophys. Research, v. 84, p. 4533–4536.
McMillan, P., 1985, Vibrational spectroscopy in the mineral sciences: Rev. Mineralogy, 14, p. 9–64.
Megaw, H. D., 1974, The seven phases of sodium niobate: Ferroelectrics, v. 7, p. 87–89.
Mysen, B. O., Virgo, D., and Seifert, F. A., 1985, Relationships between properties and structure of aluminosilicate melts: Am. Mineralogist, v. 70, p. 88–105.
Newton, M. D., O'Keeffe, M., and Gibbs, G. V., 1980, Ab initio calculation of interatomic force constants in $H_6Si_2O_7$ and the bulk modulus of α quartz and α cristobalite: Physics Chemistry Minerals, v. 6, p. 305–312.
O'Keeffe, M., Domenges, B., and Gibbs, G. V., 1985, Ab initio molecular orbital calculations on phosphates: Comparison with silicates: Jour. Phys. Chemistry, v. 89, p. 2304–2309.
O'Keeffe, M., and Hyde, B. G., 1981, The role of nonbonded forces in crystals; *in*, Navrotsky, A., and O'Keeffe, M., eds., Structure and Bonding in Crystals: New York, Academic Press, v. 1, p. 227–254.
Pauling, L., 1929, The principles determining the structure of complex ionic crystals: Am. Chem. Soc. Jour. v. 51, p. 1010–1026.
———— 1960, The Nature of the Chemical Bond, 3d ed.: Ithaca, N.Y., Cornell Univ. Press, 644 p.
Pfeiffer, P., 1916, Die Krystalle als Molekulverbindungen II: Zeitschr. Anorg. Allg. Chemistry, v. 97, p. 161–174.

Prewitt, C. T., Sueno, S., and Papike, J. J., 1976, The crystal structures of high albite and monalbite at high temperature: Am. Mineralogist, v. 61, p. 1213–1225.
Ralph, R., and Ghose, S., 1980, Enstatite, $Mg_2Si_2O_6$: compressibility and crystal structure at 21 kbar: Am. Geophys. Union Trans., v. 61, p. V174.
Robinson, G. R., and Haas, J. L., Jr., 1983, Heat capacity, relative enthalpy, and calorimetric entropy of silicate minerals: an empirical method of prediction: Am. Mineralogist, v. 68, p. 541–553.
Robinson, K., Gibbs, G. V., and Ribbe, P. H., 1971, Quadratic elongation: a quantitative measure of distortion in coordination polyhedra: Science, v. 172, p. 567–570.
Shannon, R. D., 1976, Revised effective ionic radii and systematic studies of interatomic distance in halides and chalcogenides: Acta Cryst., v. A32, p. 751–767.
Sharp, Z. D., Hazen, R. M., and Finger, L. W., 1987, High-pressure crystal chemistry monticellite, $CaMgSiO_4$: Amer. Mineralogist, v. 72, p. 748–755.
Swanson, D. K., and Peterson, R. C., 1980, Polyhedral volume calculations: Canadian Mineralogist, v. 18, p. 153–156.
Toraya, H., Iwai, S., Marumo, F., and Hirao, M., 1977, The crystal structure of taeniolite, $KLiMg_2Si_4O_{10}F_2$: Zeitschr Krist., v. 146, p. 73–83.
———— 1978, The crystal structure of a Germanate mica, $KMg_3Ge_3Al0_{10}F_2$: Mineralog. Jour. (Japan), v. 9, p. 221–230.
Vaughan, M. T., and Guggenheim, S., 1986, Elasticity of muscovite and its relationship to crystal structure: Jour. Geophys. Research, v. 91, p. 4657–4664.
Vaughan, M. T., and Weidner, D. J., 1978, The relationship of elasticity and crystal structure in andalusite and sillimanite: Physics Chemistry Minerals, v. 3, p. 133–144.
Vegard, L., and Dale, H., 1928, Untersuchungen ueber Mischkristalle und Legierungen: Zeitschr. Krist., v. 67, p. 148–162.
Weidner, D. J., Wang, H., and Ito, J., 1978, Elasticity of orthoenstatite: Phys. Earth Planetary Int., v. 17, p. P7–P13.
Yoon, H. S., and Newnham, R. E., 1973, The elastic properties of beryl: Acta Cryst., v. A29, p. 507–509.
Zhang, Z. G., Boisen, M. B., Jr., Finger, L. W., and Gibbs, G. V., 1985, Molecular mimicry of the geometry and charge density distribution of polyanions in borate minerals: Am. Mineralogist, v. 70, p. 1238–1247.