American Mineralogist, Volume 66, pages 819–826, 1981

The role of the BeOSi bond in the structures of beryllosilicate minerals

JAMES W. DOWNS AND G. V. GIBBS

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

Ab initio STO-3G molecular orbital methods have been used to calculate equilibrium geometries for the dimers, $BeSi(OH)_7$ and H_6BeSiO_7, to model the BeOSi bonds in beryllosilicate minerals. The optimized geometry and calculated potential energy surface for the dimer $BeSi(OH)_7$ are consistent with the Be–O and Si–O bridging bond length and BeOSi angle variations observed for these minerals. This indicates that the structures of beryllosilicates are determined in part by the same kind of short range forces that govern the geometry of the BeOSi bond in the dimer. Calculations for H_6BeSiO_7 indicate that the BeOSi angle is an intrinsic consequence of the electronic structure of the BeOSi bond and not merely a property of the coordination number of the bridging oxygen. The calculations also indicate that coupled substitutions of Be for either Si or Al will tend to occur in silicate structures that have TOT angles near the calculated equilibrium value (129°) for the BeOSi angle.

A refinement of the anisotropic temperature factors and $\Delta\rho$ maps of asbecasite, $Ca_3(Ti,Sn)As_6Si_2Be_2O_{20}$, calculated with the published data of Cannillo *et al.* (1969) indicate that the BeOSi bond in the mineral may not be straight as reported. The potential energy surface for H_6BeSiO_7 appears to conform with the anisotropic charge density distribution observed for the BeOSi bond in asbecasite. When the short Be–O bond in the mineral is omitted from a regression analysis of experimental data, only two percent of the variation in d(Be–O) can be explained in terms of a linear dependence on the BeOSi angle.

Introduction

More than 40 beryllium minerals have been described in the literature of which more than half are silicates (Ross, 1964). In minerals, Be has thus far only been observed in tetrahedral coordination with O, OH, or F as ligands. Although triangular BeO_3 groups have been observed in the synthetic phases $Ca_{12}Be_{17}O_{29}$, Y_2BeO_4, $SrBe_3O_4$ (Harris and Yakel, 1966, 1967, 1969), and $Rb_2Be_2Si_2O_7$ (Howie and West, 1977), it has been argued that these phases may be metastable (Harris and Yakel, 1969). Beryllium plays a crystal chemical role in minerals similar to that of Si. Indeed, isomorphous substitution of as much as 0.1 weight percent Be for the tetrahedral cations in garnets, pyroxenes, amphiboles, micas, and feldspars is known. Silicates containing substantial amounts of Be, however, tend to adopt structures unique to beryllosilicates.

A prominent structural feature of beryllosilicates is the BeOSi bond. It is likely that the configuration of a beryllosilicate structure is governed in part by the inherent geometry of this bond as it often embodies the dominant bonding forces in the crystal. In this paper, the energetics of two beryllosilicate dimers, $BeSi(OH)_7$ and H_6BeSiO_7, are investigated with *ab initio* self-consistent field (SCF) molecular orbital (MO) calculations to determine the extent to which their minimum energy geometries mimic the observed bond lengths and angles of BeOSi bonds in beryllosilicate minerals (Downs, 1980).

Molecular orbital model

Although silicates have traditionally been regarded as ionic compounds (Verhoogen, 1958; Clark *et al.*, 1969; Gait and Ferguson, 1970; Appelo, 1977), it has been argued by Pauling (1939) that the Si–O bond is as much covalent as ionic in nature. This argument is based on the notion that the electronegativity difference between bonded atoms is a measure of the covalency of the bond. Similar arguments sug-

0003–004X/81/0708–0819$02.00

gest that the Be–O bond is also substantially covalent (40–60%). Furthermore, experimental charge deformation maps through BeOSi units in euclase, $AlBeSiO_4(OH)$, show a significant accumulation of electron density in the bonds, indicating that both the Be–O and the Si–O bonds possess significant covalent character (Downs, 1980; Downs *et al.*, 1981). Since these bonds are indicated to be substantially covalent, any formalism used to calculate the total energy of systems containing the bonds should include interactions of a covalent as well as ionic nature.

In a purely ionic model, only coulombic interactions between charged atomic centers are considered. Since covalency indicates sharing of electrons between bonded centers, a method that optimizes the electron distribution is required to model covalent effects. Clearly the calculation of the total wave function of the system is most desirable inasmuch as such a method would model ionic, as well as covalent interactions since both depend ultimately upon the electron distribution. Molecular orbital (MO) methods satisfy this criterion in that the total wave function Ψ of the system is approximated by a product of one electron MO's expressed as

$$\Psi = \prod_{i=1}^{n} \phi_1\phi_2 \cdots \phi_n \qquad (1)$$

where the ϕ_i's have been "antisymmetrized" with respect to the permutation of electrons to be consistent with the Pauli exclusion principle. These MO's are in turn approximated by a linear combination of atomic orbitals (LCAO) as in

$$\phi_i = \sum_k c_{ik}\chi_k \qquad (2)$$

where the MO coefficients c_{ik} are obtained by the iterative self-consistent solution of the Roothaan equations. In *ab initio* MO theory all resulting matrix elements are accurately evaluated. In these calculations the atomic orbital (AO) basis functions χ_k are represented by Slater Type Orbitals (STO's) which are approximated by a linear combination of Gaussian functions denoted STO-NG, where N is the number of Gaussians used in the expansion. In this study each STO was represented by a linear combination of three Gaussian functions denoted STO-3G. Although an infinite AO basis set is required to reach the Hartree–Fock limit, we have used a minimal basis set (Hehre *et al.*, 1969, 1970) which has been found useful in providing insight into the nature of the bonding forces in minerals (Sauer and Zurawski, 1979; Newton and Gibbs, 1979, 1980; Meier and Ha, 1980; Swanson, 1980; Chakoumakos, 1981; Gupta *et al*, 1981; Gibbs *et al.*, 1981).

In this study, our main purpose is to calculate the total energy E for the molecule in question. Recalling the Schrödinger equation,

$$H\Psi = E\Psi \qquad (3)$$

where H is the Hamiltonian operator, multiplying both sides by the complex conjugate of the wave function Ψ^*, and integrating over all spatial coordinates yields

$$E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \qquad (4)$$

such that the total energy E is the expectation value of the Schrödinger Hamiltonian. The correct wave function for a molecule of fixed geometry is obtained using the variation theorem of quantum mechanics which states that the energy calculated using the equations of quantum mechanics with the use of the correct wave function Ψ_{real} for the ground state of the system is less than that calculated with any other wave function Ψ that might be proposed. Using this technique then to calculate the total energy for a given geometry, we may then vary the geometry (usually within certain symmetry constraints) and thus find the lowest possible energy, as well as the "optimized" geometry for the molecule. The calculations reported in this paper were completed using the Pople *et al.* (1973) GAUSSIAN 70 computer program (QCPE, 11, 236).

Theoretical and experimental chemistry of the BeOSi bond

The equilibrium geometry of the BeOSi bond

The BeOSi bonds of the dimers $BeSi(OH)_7$ and H_6BeSiO_7 were chosen as models for the corresponding bonds in the beryllosilicates. In the study, the bond lengths and bridging angle for each dimer were optimized within the constraint of C_s symmetry with the terminal OH bonds fixed at 0.96Å, and the OTO and TOH angles fixed at 109.47°. The resulting geometries are shown in Figure 1.

The bridging oxygen of $BeSi(OH)_7$ is clearly overbonded with $p_0 = 2.5$ (where p_0 is the Pauling bond strength sum to oxygen) whereas that of H_6BeSiO_7 is underbonded with $p_0 = 1.5$. As expected the bridging bonds are longer in the overbonded case relative to the underbonded case. The mean bridging bond lengths calculated for the two dimers (tantamount to

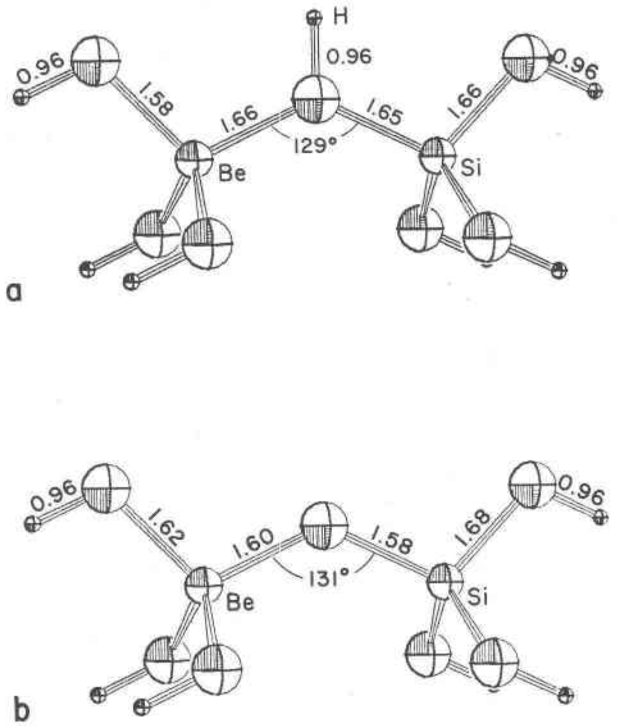
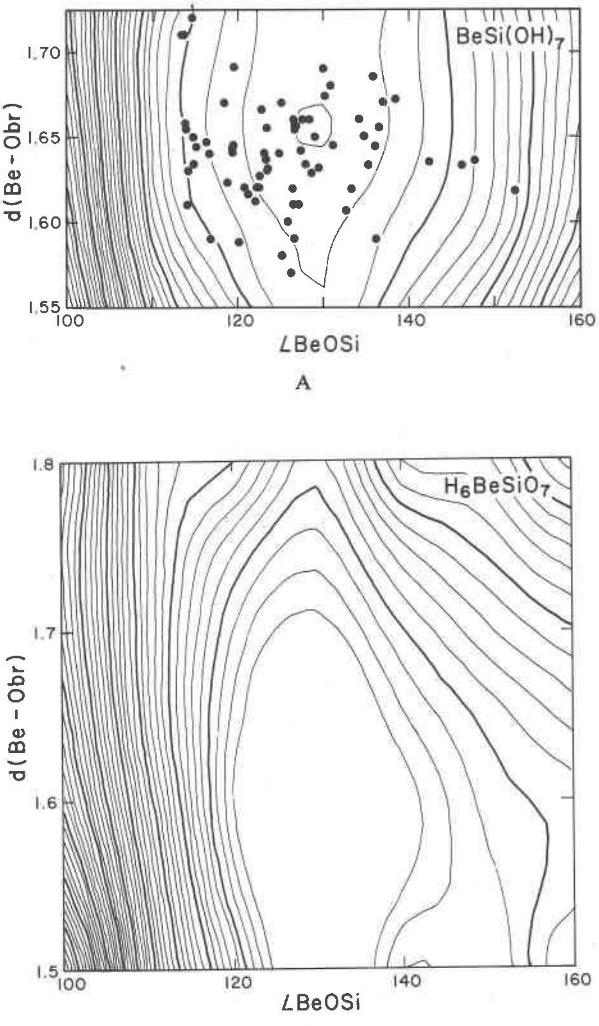


Fig. 1. Optimized geometries for (a) $BeSi(OH)_7$ and (b) H_6BeSiO_7, calculated using *ab initio* theory with a minimal STO-3G basis. *Large spheres* represent oxygen, *small spheres* represent hydrogen; no significance is attached to the relative sizes of these spheres. Angles O–Be–O = O–Si–O = 109.47°, d(O–H) = 0.096Å. During optimization, four sets of bond lengths were independently varied, namely non-bridging Be–O and Si–O, and bridging Be–O and Si–O. Both molecules are in doubly eclipsed conformation with C_s symmetry.

interpolating to $p_0 = 2.0$) are ⟨d(Be–O)⟩ = 1.63Å and ⟨d(Si–O)⟩ = 1.62Å, in exact agreement with bond distances calculated using the Shannon and Prewitt radii (1969). Since the Shannon–Prewitt radii give good estimates of observed bond lengths, our results indicate that the BeOSi bond in beryllosilicates may be adequately modeled with small BeOSi containing dimers when using *ab initio* methods.

In most beryllosilicates, the bridging oxygen of the BeOSi bond is either bonded to another fairly electronegative atom (*e.g.*, Al, Be) or it is bonded to one or more electropositive atoms (*e.g.*, Ca, Na). A two-coordinated bridging oxygen involved in a BeOSi bond is extremely rare (*e.g.*, asbecasite, Cannillo *et al.*, 1969). Thus, the dimer $BeSi(OH)_7$ whose bridging oxygen is bonded to Be, Si, and H is possibly the simplest model for the BeOSi bonds observed in most beryllosilicates.

The total energy for $BeSi(OH)_7$ and H_6BeSiO_7 when plotted as a function of bridging Be–O bond length and angle results in the potential energy surfaces shown in Figure 2a and 2b, respectively. Examination of the surface for $BeSi(OH)_7$ indicates that the total energy varies rapidly with angle but slowly with bond length. Hence, we may expect to observe a fairly wide range of Be–O bridging bond lengths and a relatively narrow range of BeOSi angles in beryllosilicates. This is in contrast to the behavior of the Si–O–Si bond.



A

B

Fig. 2. Potential energy as a function of Be–O bridging bond length, d(Be–Obr), and bridging angle BeOSi for (a) $BeSi(OH)_7$ and (b) H_6BeSiO_7 calculated with all non-bridging bonds and the Si–O bridging bond fixed at the optimized values. One contour = 0.001 atomic units = 0.63 kcal = 2.63 kJ. The Be–O bridging bond length and angle data from 28 beryllosilicate structure refinements are shown as dots in (a). The mean values for these data are ⟨d(Be–Obr)⟩ = 1.64Å and ⟨BeOSi⟩ = 126°.

A comparison of experimental and theoretical SiOBe geometries

It has been proposed by Ganguli (1979) that a correlation obtains between Be–O bridging bond length and BeOSi angle with wider angles involving shorter bonds. The fact that the minimum energy portion of the potential energy surface for $BeSi(OH)_7$ forms a narrow valley symmetric about BeOSi angle = 130° indicates that no such correlation should exist. It is noteworthy that a similar potential energy surface calculated for the dimer $H_6Si_2O_7$ (Meagher *et al.*, 1980; Gibbs *et al.*, 1981) shows that the energy varies rapidly with Si–O bond length but slowly with SiOSi angle, just opposite to that calculated here for $BeSi(OH)_7$. The $H_6Si_2O_7$ potential energy surface has been shown to be consistent with the observed Si–O bridging bond length and angle variations in the silica polymorphs and siloxanes (Newton and Gibbs, 1980; Meagher *et al.*, 1980; Gibbs *et al.*, 1981). When the bridging Be–O bond lengths and angles from observed structures are plotted on the potential energy surface for $BeSi(OH)_7$ a wide scatter of values obtains with the bond lengths varying between 1.56Å and 1.72Å and most of the angles varying between 115° and 140°. The mean values for these data are $\langle d(\text{Be–O})\rangle$ = 1.64Å and $\langle \text{BeOSi}\rangle$ = 126° which agree with the values (1.66Å, 129°) optimized for $BeSi(OH)_7$. This result is consistent with an observation made previously by Brown and Gibbs (1970) that Be tends to be involved in narrow TOT angles. The agreement between calculated and observed values indicates that the observed geometries of BeOSi bonds are governed mainly by the local bonding forces within these units themselves rather than by the long range forces of the crystal field.

Figure 2a includes data from three-membered tetrahedral rings (*e.g.*, euclase and phenacite) which tend to cluster in the narrow angle range (Downs, 1980). It is noteworthy that three-membered tetrahedral rings are relatively common in beryllosilicates. In contrast, they are relatively uncommon in silicates because of the inherent instability of the narrow SiOSi angles (approximately 126°) required to form such a ring (Chakoumakos and Gibbs, 1980; Chakoumakos, 1981; Chakoumakos *et al.*, 1981). The inherent tendency of the BeOSi bond to adopt an angle of 129° indicates that three-membered beryllosilicate rings are unstrained. On the other hand, when the ring consists of three silicate tetrahedra, it represents a strained configuration because of the inherent tendency of the disiloxy unit to adopt an angle of 145° (Newton and Gibbs, 1980; Chakoumakos and Gibbs, 1980; Chakoumakos, 1981; Chakoumakos *et al.*, 1981). Cases where a bridging oxygen is bonded to two edge-sharing Be tetrahedra and one Si tetrahedron, as in epididymite, require narrow BeOBe angles with a concomitant widening of the BeOSi angles. Data from such topologies tend to cluster near the wide angle range of the stable region. Thus it appears that whatever topology is adopted by the tetrahedral frame of a beryllosilicate that the resulting BeOSi angles should correspond to the minimum energy region of the potential energy surface for $BeSi(OH)_7$.

A linear regression analysis calculated for the data in Figure 2a yields an r^2 value of only 0.02, suggesting that only two percent of the variation in d(Be–Obr) can be explained in terms of a linear dependence on the BeOSi angle. This result is contrary to that obtained by Ganguli (1979) who calculated an r^2 value of 0.35 for this correlation. Our data are somewhat more extensive than those used by Ganguli and we have excluded a questionable point for asbecasite at d(Be–O) = 1.53Å and BeOSi angle = 180° on which his proposed correlation is highly dependent. If the correlation is real, we might expect that it would persist with the omission of this one point. Inasmuch as our data (Fig. 2a) show a relatively wide scatter, we suggest that the evidence for such a correlation is lacking.

The BeOSi angle dependence on the coordination number of the bridging oxygen

We will now examine the extent to which the equilibrium BeOSi angle may depend on the fact that the bridging oxygen of $BeSi(OH)_7$ is three-coordinated. To investigate this dependence we examined the optimized geometry and potential energy surface for H_6BeSiO_7 (which is essentially $BeSi(OH)_7$ with the hydrogen removed from the bridging oxygen). The fact that the optimized BeOSi angle of 131° is practically the same as that calculated for $BeSi(OH)_7$ indicates that the preference for the BeOSi angles in beryllosilicates to be bent is not merely a proclivity of the bridging oxygen to form more bonds in order to satisfy its valence. The potential energy surface for H_6BeSiO_7 is quite similar to that for $BeSi(OH)_7$ at narrow angles; however, at wide angles, the H_6BeSiO_7 surface is less steep. This result indicates that although the equilibrium BeOSi angle with a two-coordinated bridging oxygen is 131°, the energy barrier to widening the angle is less than for a three-coordinated oxygen. In other words, if a BeOSi angle wider than 131° were required in order to satisfy steric constraints this could be accommodated with minimal destabilization of the structure. The shape of the H_6BeSiO_7 surface also hints at the existence of a possible weak correlation between d(Be–Obr) and angle BeOSi when the oxygen is two-coordinated. However, the paucity of two-coordinated oxygens bridging Be and Si tetrahedra makes it impossible at this time to investigate this suggestion.

$BeSi(OH)_7$ and H_6BeSiO_7 are similar to the dimers SiH_3OHBeH_3 and SiH_3OBeH_3 studied by Tossell and Gibbs (1978) using the CNDO/2 MO method. In their calculations none of the bond lengths were optimized because of the limitations of the method. The minimum energy BeOSi angles reported are 124° and 114° for the three-coordinated and two-coordinated oxygen, respectively. Tossell and Gibbs (1978) ascribe the calculated angles to the underbonded (or overbonded) nature of the bridging oxygen and indicate that the two dimers may be poor models for beryllosilicate systems. The optimized angles of 124° and 114° calculated for the two dimers were considered to be fortuitous and unrealistic. It appears that the use of TH_3O tetrahedra together with the limitations of the CNDO/2 method may have an even greater effect upon the optimized angle than the overbonded or underbonded nature of the bridging oxygen.

Calculations were also completed for both $BeSi(OH)_7$ and H_6BeSiO_7 where all bond lengths were fixed at the optimized values and the BeOSi angle was varied from 100° to 180° resulting in the energies listed in Table 1. The shapes of the resulting potential energy curves for the two dimers are compared by subtracting each energy from that calculated at angle BeOSi = 180° for each dimer in turn and plotting the values *vs.* angle BeOSi as shown in Figure 3. Using data at, and adjacent to, the energy minimum, the calculated quadratic bending force constant (given as the second derivative of the total energy function scaled by the inverse product of the two bond lengths forming the angle) for the BeOSi angle is 14 Nm^{-1} for both $BeSi(OH)_7$ and H_6BeSiO_7. The reason for this equality is evident from Figure 3 which shows the curves to be nearly identical in shape near the minimum energy. At angles wider than 130°, however, the similarity disappears in that the energy changes much more rapidly for $BeSi(OH)_7$ than for H_6BeSiO_7. The resulting difference in depth of these potential energy wells is manifest in the calculated barrier to linearity of 32 kT at room temperature for $BeSi(OH)_7$ compared to that of 8 kT calculated for H_6BeSiO_7. This difference simply reflects the improbability of a BeOSi unit adopting a

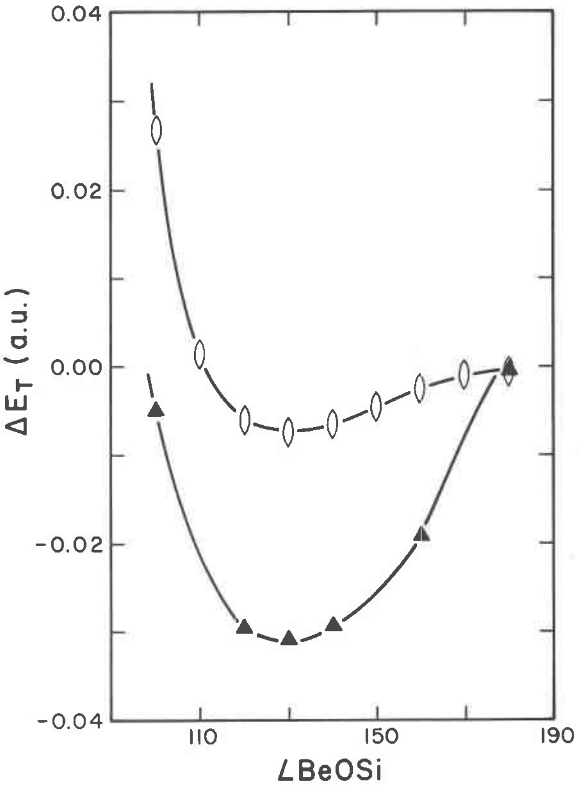


Fig. 3. Potential energy curves, $\Delta E_T = E(180°) - E(\angle BeOSi)$ atomic units), as a function of BeOSi angle in $BeSi(OH)_7$ (triangles) and H_6BeSiO_7 (diads) with bond lengths fixed at the optimized values. The calculated quadratic bending force constant for both molecules is 14 Nm^{-1}. The barrier to linearity is 32 kT for $BeSi(OH)_7$ and 8 kT for H_6BeSiO_7 at 300 K.

Table 1. The total energy, E_T (atomic units), calculated as a function of angle BeOSi for $BeSi(OH)_7$ and H_6BeSiO_7. Bond lengths were fixed at the optimized values shown in Figure 1 for these calculations. One atomic unit = 627.5 kcal = 2625.46 kJ.

$BeSi(OH)_7$			
100	-821.01221	140	-821.03647
120	-821.03684	160	-821.02626
130	-821.03809	180	-821.00731
		$\angle BeOSi_e$ = 129°	
H_6BeSiO_7			
100	-820.14048	150	-820.17163
110	-820.16581	160	-820.16951
120	-820.17303	170	-820.16796
130	-820.17457	180	-820.16740
		$\angle BeOSi_e$ = 131°	

straight BeOSi angle when the bridging oxygen is three-coordinated.

The curve for H_6BeSiO_7 is similar to that calculated by Newton and Gibbs (1980) for $H_6Si_2O_7$. Using the energies from the curve for $BeSi(OH)_7$, a Boltzmann distribution curve was calculated. This is shown together with a frequency plot (using the data in Fig. 2a) of the observed BeOSi angles in Figure 4. The frequency distribution is similar to that reported by Tossell and Gibbs (1978). The Boltzmann distribution curve is a plot of the function $\exp[-\Delta E(\angle BeOSi)/kT]$ where T = 300 K.

Examination of the linear BeOSi bond in asbecasite

The structure of asbecasite, $Ca_3(Ti,Sn)As_6Si_2Be_2O_{20}$ solved from 3-dimensional film data, was refined by least-squares methods to R = 0.066 for all data using isotropic temperature factors on each atom and a correction for isotropic extinction (Cannillo *et al.,* 1969). Our attention is drawn to this structure because of the short Be–O (1.53Å) and Si–O (1.58Å) bonds, the wide BeOSi angle of 180°, and the fact that the bridging oxygen is two-coordinate. Our calculations on H_6BeSiO_7 indicate that a bent bond configuration is considerably more stable than a straight one. An investigation of the isotropic temperature factor for the BeOSi bridging O(4) oxygen of asbecasite shows it to be nearly twice the mean value of the other oxygen thermal parameters. This suggests that the short bond lengths and wide angle may be due in part to averaged positional disorder at the bridging oxygen atom. The structure was refined by Cannillo *et al.* (1969) in space group $P\bar{3}c1$ with Be, O(4), and Si located on a three-fold symmetry axis requiring the BeOSi angle to be straight.

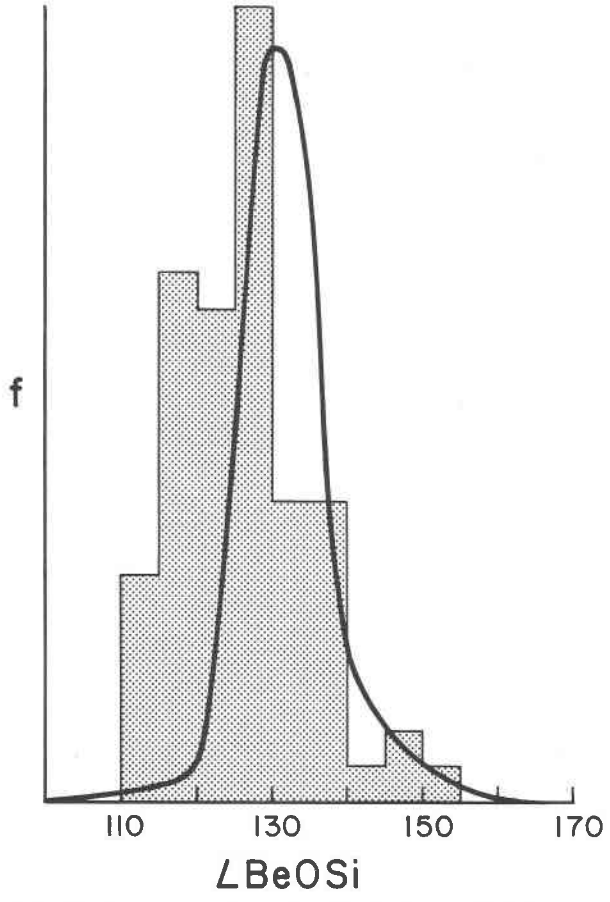


Fig. 4. Frequency of BeOSi angles (f) in beryllosilicates *vs.* angle BeOSi with Boltzmann distribution curve calculated for $BeSi(OH)_7$ from energies listed in Table 1.

Using the reported structure factors, we attempted a further refinement of the structure of asbecasite by expanding the calculation to include a refinement of the anisotropic temperature factors for each atom. After a full matrix refinement using isotropic temperature factors converged to R = 0.06 for all data, a difference Fourier ($\Delta\rho$) map calculated through the Be–O(4)–Si linkage showed conspicuous anisotropy of charge density at the site of O(4) normal to the three-fold axis. In addition, anisotropy in the charge density parallel to the symmetry axis is exhibited by Be and Si. The introduction of anisotropic thermal parameters for O(4) alone yielded $U_{11} = U_{22} = 0.0120$ and $U_{33} = 0.0089$. The introduction of anisotropic temperature factors for Si gave $U_{11} = U_{22} = 0.0028$ and $U_{33} = 0.0047$. Attempts at full matrix refinement failed because the anisotropic temperature factors on several atoms (notably Be) were calculated as non-positive definite. Since we were using a data set averaged for $P\bar{3}c1$ symmetry, it was impossible to complete a refinement for the structure with the three-fold axis removed. An analysis of the atom shifts due to positional disorder from the $\Delta\rho$ map indicates that the Be–O(4)–Si angle may be close to 150–160° rather than 180° as reported. Although this angle is still at the wide angle limit of observed BeOSi angles, the potential energy curve for H_6BeSiO_7 suggests that when the bridging oxygen is two-coordinated that wide angles are nearly as stable as that of equilibrium angle of 131°. The gentle slope of the H_6BeSiO_7 potential energy curve at wide angles indicates that a two-coordinated oxygen involved in a wide BeOSi angle may tend to exhibit increased anisotropic motion and positional disorder relative to a similar oxygen involved in a narrow

BeOSi angle (*i.e.,* the quadratic bending force constant for the BeOSi angle is not constant but decreases in a regular way with widening angle when the bridging oxygen is two-coordinated).

Conclusions

Ab initio generated equilibrium geometries and potential energy surfaces calculated for $BeSi(OH)_7$ and H_6BeSiO_7 are consistent with observed variations in Be–O and Si–O bridging bond lengths and angles BeOSi in beryllosilicates. These results suggest that the configuration of the tetrahedral frame of a beryllosilicate may depend in large measure upon the tendency for individual BeOSi bonds to adopt equilibrium geometries. The narrow nature of the resulting equilibrium BeOSi angles may permit structural units unstable in pure silicate systems (*e.g.,* three-membered rings) to be stabilized in beryllosilicates. We may further expect beryllium not to participate extensively in coupled substitutions for Si or Al in structures that require large BeOSi angles (*e.g.,* alkali feldspars). Rather we may expect such substitution to occur in structures where TOT angles near the equilibrium value for BeOSi predominate (*e.g.,* cordierite, willemite).

Acknowledgments

It is a pleasure to thank the National Science Foundation for supporting this investigation with grant EAR-7723114 to G.V. Gibbs and P.H. Ribbe to study bonding in minerals. We are also pleased to acknowledge VPI & SU for promoting the development and growth of an excellent University Computing Center and for contributing large sums of money to help defray the computing costs incurred in the molecular orbital calculations. We thank Ramonda Haycocks for typing the manuscript and Sharon Chiang for her deftness in drafting the figures for this paper.

References

Appelo, C. A. J. (1977) Layer deformation and crystal-energy of trioctahedral 1M-micas and related minerals. Proceedings 2nd International Symposium on Water–Rock Interaction, Strasbourg, Ms.

Brown, G. E., and Gibbs, G. V. (1970) Stereochemistry and ordering in the tetrahedral portion of silicates. The American Mineralogist, 55, 1587–1607.

Cannillo, E., Giuseppetti, G., and Tadini, C. (1969) The crystal structure of asbecasite. Accademia Nazionale dei lincei, Estratto dai Rendiconti della classe di Scienze fisiche, Matematiche e naturali, serie VIII, vol. XLVI, fasc. 4, 457–467.

Chakoumakos, B. C. (1981) A molecular orbital study of I. Rings in silicates and siloxanes and II. Order-disorder isomorphism in silicates. M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Chakoumakos, B. C., and Gibbs, G. V. (1980) A molecular orbital study of silicate tetrahedral rings (abstr.). Geological Society of America Abstracts with Programs, 12, 400.

Chakoumakos, B. C., Hill, R. J., and Gibbs, G. V. (1981) A molecular orbital study of rings in silicates and siloxanes. The American Mineralogist, 66, in press.

Clark, J. R., Appleman, D. E., and Papike, J. J. (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. Mineralogical Society of America Special Paper, 2, 31–50.

Downs, J. W. (1980) Bonding in beryllosilicates: The charge density of euclase, $AlBeSiO_4(OH)$, and molecular orbital studies of beryllium oxyanions. M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Downs, J. W., and Gibbs, G. V. (1980) Calculation of tetrahedral Be-O bridging bond lengths and angles (abstr.). Geological Society of America Abstracts with Programs, 12, 416.

Downs, J. W., Hill, R. J., Newton, M.D., Tossell, J. A. and Gibbs, G. V. (1981) Theoretical and experimental charge density distributions in silicates. In, P. Coppens and M. B. Hall, Eds., Electron Distributions and the Chemical Bond. Plenum Press, New York.

Gait, R. I., and Ferguson, R. B. (1970) Electrostatic charge distributions in the structure of low albite. Acta Crystallographica, B26, 68–71.

Ganguli, D. (1979) Variability in interatomic distances and angles involving BeO_4 tetrahedra. Acta Crystallographica, B35, 1013–1015.

Gibbs, G. V., Meagher, E. P., Newton, M. D., and Swanson, D. K. (1981) A comparison of experimental and theoretical bond length and angle variations for minerals, inorganic solids and molecules. In M. O'Keeffe and A. Navrotsky, Eds., Structure and Bonding in Crystals. Academic Press, New York.

Gupta, A., Swanson, D. K., Tossell, J. A., and Gibbs, G. V. (1981) Calculation of bond distances, one-electron energies, and electron density distributions in first-row tetrahedral hydroxy and oxyanions. The American Mineralogist.

Harris, L. A., and Yakel, H. L. (1966) The crystal structure of calcium beryllate, $Ca_{12}Be_{17}O_{29}$. Acta Crystallographica, 20, 295–301.

Harris, L. A., and Yakel, H. L. (1969) The crystal structure of $SrBe_3O_4$. Acta Crystallographica, B25, 1647–1651.

Harris, L. A., Yakel, H. L. (1967) The crystal structure of Y_2BeO_4. Acta Crystallographica, 22, 354–360.

Hehre, W. T., Ditchfield, R., Stewart, R. F., and Pople, J. A. (1970) Self-consistent molecular orbital methods. IV. Use of Gaussian expansions of Slater-type orbitals. Extension to second row molecules. Journal of Chemical Physics, 52, 2769–2773.

Hehre, W. T., Stewart, R. F., and Pople, J. A. (1969) Self-consistent molecular orbital methods. I. Use of Gaussian expansions of Slater-type atomic orbitals. Journal of Chemical Physics, 51, 1657–2664.

Howie, R. A., and West, A. R. (1977) The crystal structure of $Rb_2Be_2S_{12}O_7$. Acta Crystallographica, B33, 381–385.

Meagher, E. P., Swanson, D. K., and Gibbs, G. V. (1980) The calculation of tetrahedral Si–O and Al–O bridging bond lengths and angles. EOS, 61, 408.

Meier, R., and Ha, T. (1980) A theoretical study of the electronic structure of disiloxane [$(SiH_3)_2O$] and its relation to silicates. Physics and Chemistry of Minerals, 6, 37–46.

Newton, M. D., and Gibbs, G. V. (1980) *Ab initio* calculated geometries and charge distributions for H_4SiO_4 and $H_6Si_2O_7$ compared with experimental values for silicates and siloxanes. Physics in Chemistry of Minerals, 6, 221–246.

Pauling, L. (1939) The Nature of the Chemical Bond, 1st Ed. Cornell University Press, Ithaca, New York.

Pople, J. A., Hehre, W. J., Lathan, W. A., Ditchfield, R., Newton, M. D. (1973) GAUSSIAN 70: *Ab initio* SCF-MO calculations on organic molecules. Quantum Chem. Progr. Exch., 11, 236. Univ. Indiana, Bloomington.

Ross, M. (1964) Crystal chemistry of beryllium. United States Geological Survey Professional Paper 468.

Sauer, J., and Zurawski, B. (1979) Molecular and electronic structure of disiloxane. An *ab initio* study. Chemical Physics Letters, 65, 587–591.

Shannon, R. D., and Prewitt, C. T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B25, 925–945.

Tossell, J. A., and Gibbs, G. V. (1978) The use of molecular-orbital calculations on model systems for the prediction of bridging-bond-angle variations in siloxanes, silicates, silicon nitrides, and silicon sulfides. Acta Crystallographica, A34, 463–472.

Verhoogen, J. (1958) Physical properties and bond type in Mg–Al oxides and silicates. The American Mineralogist, 43, 552–579.

Manuscript received, February 13, 1981;
accepted for publication, March 24, 1981.