

## Variations of bond lengths and volumes of silicate tetrahedra with temperature

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### ABSTRACT

The apparent SiO bond lengths recorded for silicates over a range of temperatures either typically are invariant or exhibit a contraction with increasing temperature. A rigid-body thermal analysis was completed for the tetrahedra in nine silicates whose structures have been determined over a range of temperatures from 15 to 1250 K and whose tetrahedra seem to behave as rigid units. The coordinates provided by the analysis yield bond lengths and polyhedral volumes corrected for the librational motion of each silicate tetrahedron. The bond lengths and volumes estimated for tetrahedra with four bridging O atoms seem to increase with temperature at a faster rate than those with four nonbridging O atoms. Those for tetrahedra with two or three nonbridging O atoms tend to increase at an intermediate rate. An analysis of the rigid-body motion of coordinated polyhedra yields a simple but accurate expression for correcting bond lengths for thermal vibrations. It also indicates that the temperature factors of the coordinating anions of rigid polyhedra should be larger than those of the coordinated cations, regardless of the masses of the constituent atoms.

### INTRODUCTION

The atoms of a crystal are never at rest but are in perpetual oscillatory motion about their equilibrium positions with their mean square displacement amplitudes, MSDAs, increasing with temperature. A structural analysis of a crystal by diffraction methods can yield a set of precisely determined mean positional coordinates for each of its nonequivalent atoms, but, because of the oscillatory motions of the atoms, the separations calculated from these coordinates, referred to as the apparent interatomic separations,  $R$ , are always less than the mean interatomic separations,  $R_m$  (Cruickshank, 1956, 1961; Busing and Levy, 1964). It is the mean interatomic separations that have chemical significance, as they are the bonded and nonbonded mean interatomic separations that exist between atoms at their equilibrium positions.

As observed by Busing and Levy (1964), before an estimate can be made of the mean interatomic separation between a pair of atoms, a knowledge is required of the correlations among the respective motions of these atoms. Unfortunately, of the possible correlated motions, only a few are sufficiently well understood so that a mean interatomic separation can be accurately estimated. One such motion is the rigid-body motion often exhibited by the atoms of a molecule that are strongly linked together and that exhibit both translational and librational (rotatory) modes of oscillations (Cruickshank, 1957; Willis and Pryor, 1975). Accurate estimates of the mean interatomic separations for such a rigid molecule can be obtained from a TLS (translational, librational, and screw modes

of motion) modeling of the thermal motion (Cruickshank, 1957; Schomaker and Trueblood, 1968). Not only do the separations calculated from the atomic coordinates determined for molecular crystals provided by the analysis tend to be in good agreement with those obtained by spectroscopic methods (Dunitz et al., 1988), but also the lengths of bonds that have similar strengths tend to show a relatively narrow range of values.

In recent studies of the MSDAs observed for the Si and O atoms in a number of ordered framework silicate minerals, Bürgi (1989), Downs (1989), Downs et al. (1990), and Armbruster et al. (1990) claimed that the coordinated silicate tetrahedra in these minerals seem to behave as rigid bodies. These studies indicate that the Si and O atoms move in tandem along each SiO bond so that the MSDA of Si toward O,  $z_{\text{SiO}}$ , tends to equal that of O toward Si,  $z_{\text{OSi}}$ . Downs et al. (1990) inferred from this result that the SiO bonds in these structures are oscillating back and forth as rigid units. Similar results seem to hold for the nonbonded OO separations that define the edges of each SiO<sub>4</sub> group. Furthermore, as one might expect, the MSDAs along the line of separation between a given pair of O atoms in adjacent silicate tetrahedra are not, in general, equal. On the basis of these observations, the tetrahedra in ordered framework silicates seem to behave as rigid bodies (with fixed interatomic separations) librating and translating back and forth about their equilibrium positions.

In this study, a TLS rigid-body thermal motion modeling was completed for the SiO<sub>4</sub> silicate tetrahedra in

nine selected ordered silicates whose diffraction data were recorded over a relatively wide range of temperatures. Estimates of the mean interatomic SiO separations,  $R_{\text{TLS}}(\text{SiO})$ , calculated from the coordinates obtained in the TLS analysis, yielded separations for room-temperature structure determinations that are typically about 0.005 Å longer than  $R(\text{SiO})$ , the observed apparent SiO bond length. In addition,  $R_{\text{TLS}}(\text{SiO})$  calculated for data recorded at temperatures up to 1250 K are considerably greater, by as much as 0.03 Å, than  $R(\text{SiO})$ . In fact,  $R_{\text{TLS}}(\text{SiO})$  increases or is unchanged with temperature, whereas  $R(\text{SiO})$  typically decreases or remains unchanged with increasing temperature. As a TLS analysis involves a tedious calculation, we developed a simple expression, referred to as the simple rigid bond correction, for estimating the mean interatomic separations for rigid coordinated polyhedra. Application of this correction to the nine selected silicates yielded bond lengths that match those obtained in a TLS analysis with an esd of 0.002 Å.

#### A REVIEW OF BOND LENGTH CORRECTION EXPRESSIONS

In a careful study of bond length errors ascribed to the libration of a molecule in a molecular crystal, Cruickshank (1956) showed that the positional error of an atom,  $\Delta r$ , in a radial direction can be estimated by

$$\Delta r = \frac{1}{2r} \left( \frac{s^2}{1 + s^2/q^2} + \frac{t^2}{1 + t^2/q^2} \right) \quad (1)$$

where  $r$  is the distance between the libration center of the molecule and the atom,  $s^2$  and  $t^2$  represent the librational MSDAs of the atom perpendicular to the radial direction, and  $q^2$  represents a spherical Gaussian breadth parameter fit to the electron density peak of the atom that measures translational motion only. Inasmuch as  $q^2$ ,  $s^2$ , and  $t^2$  are difficult to obtain, this equation has not found wide application. In the derivation of Equation 1, it was assumed that only the librations perpendicular to the radial direction are relevant, an assumption that is known to hold for molecules with  $\bar{1}$ ,  $\bar{3}$ ,  $\bar{6}$ , or  $\bar{4}3m$  point symmetry (Johnson, 1969a). By relaxing this assumption, Cruickshank was able to express the rigid-body motion of a molecule in a more general way in terms of two symmetric tensors, one representing the librational component,  $L$ , of the rigid-body motion and the other, the translational component,  $T$ . Since translational motion does not affect bond lengths, the librational component can be isolated and used in the expression

$$[\Delta \mathbf{v}]_c = \frac{1}{2} [(\text{trace } L)I_3 - L][\mathbf{v}]_c \quad (2)$$

to correct the Cartesian coordinates,  $[\mathbf{v}]_c$ , of the atoms. This expression is based on the assumption that the librational oscillations are not too large (<10–15°). However, Cruickshank's model did not take into account any

correlation between translational and librational modes of motion, which subsequently was called the screw mode of motion by Schomaker and Trueblood (1968). When the rigid-body parameters of a molecule are obtained in a refinement involving translational, librational, and screw motion, the elements of the resulting  $L$  matrix can be used, as defined by Equation 2, to provide thermally corrected positional coordinates for atoms in rigid molecules. Bond lengths,  $R_{\text{TLS}}$ , calculated from these coordinates have proven to be accurate estimates of the mean separations among the atoms in molecular crystals (Dunitz et al., 1988). To our knowledge, this procedure is the most accurate method known to date for estimating  $R_m$  in rigid molecules.

Perhaps the most widely used expression for correcting bond length is provided by the Busing and Levy (1964): "riding model," where one of the atoms,  $Y$ , is assumed to be strongly linked to one much heavier atom,  $X$ , upon which it appears to ride. This model is based on the assumption "that atom  $Y$  has all of the translational motion of atom  $X$  plus an additional motion uncorrelated with the instantaneous position of atom  $X$ " (Johnson, 1969b). An estimate of  $R_m$  for a pair of atoms exhibiting riding motion is given by

$$R_{\text{rid}} = R + \frac{\bar{w}_Y^2 - \bar{w}_X^2}{2R} \quad (3)$$

where  $\bar{w}_X^2$  and  $\bar{w}_Y^2$  are the average MSDAs of atoms  $X$  and  $Y$  in the plane perpendicular to the  $XY$  bond. The widespread use of the riding model may be ascribed to the relative ease with which the  $\bar{w}^2$  values can be obtained and to its success in obtaining reasonable OH bond length corrections.

#### THERMAL EXPANSION OF SILICATE TETRAHEDRA

The apparent SiO bond lengths,  $R(\text{SiO})$ , recorded for a number of silicate minerals over a variety of temperatures, typically either are invariant or show a slight contraction with increasing temperature. As an illustration of this point, the thermal expansion rates of  $R(\text{SiO})$ , as defined by the slopes of the regression lines fit to  $R(\text{SiO})$  as a function of  $T$ , are presented in Table 1 for low albite, acmite, diopside, jadeite, and spodumene, sodium fluorrichterite, potassium fluorrichterite, andalusite, and kyanite (Smith et al., 1986; Harlow and Brown, 1980; Armbruster et al., 1990; Winter et al., 1977; Clark et al., 1969; Cameron et al., 1973, 1983; Levien and Prewitt, 1981; Winter and Ghose, 1979). These minerals were chosen because the  $z_{\text{Osi}}^2$  and  $z_{\text{SiO}}^2$  values of their SiO bonds are highly correlated with  $z_{\text{Osi}}^2 \approx z_{\text{SiO}}^2$ , satisfying the criteria set forth by Downs et al. (1990). Also, the MSDAs of the O atoms, calculated along the edges of the tetrahedra, tend to be equal except at the highest temperatures. Taken together, these results indicate that the  $\text{SiO}_4$  tetrahedra in these structures behave as rigid bodies, except at high temperatures, where the rigid model may be expected to fail.

An examination of the expansion rates for the bonds in low albite and in sodium and potassium fluor-richterite indicates that they contract for the most part with increasing temperature. The rates recorded for the remaining silicates are marginally positive or zero. In a discussion of the implications of these results, Winter et al. (1977) noted that the invariant behavior of the SiO bond length with increasing temperature requires that the potential well for the bond be quadratic in nature. They also observed that the contraction of the bond with increasing temperature requires that the cubic term characterizing the anharmonic nature of the well be positive in sign. This implies that the curvature of the well increases more slowly at shorter bond lengths than it does at longer bond lengths, relative to the equilibrium bond length. Winter et al. (1977) considered both interpretations of the shape of the potential well to be unreasonable. In an attempt to resolve this problem, they corrected  $R(\text{SiO})$  and  $R(\text{AlO})$  in low albite for thermal motion, using the four equations presented by Busing and Levy (1964). These equations yield four sets of corrected bond lengths that show a range of values that differ by as much as 0.03 Å. Inasmuch as the correlated motions of the atoms in low albite were unknown, they were unable to decide which set of corrected bond lengths provides an accurate estimate of the mean bond lengths in the mineral.

As discussed earlier, recent studies of the temperature factors for the Si, Al, and O atoms of the framework silicates, including low albite, indicated that their tetrahedra behave as rigid bodies. Using the strategies employed by Downs et al. (1990) for the framework silicates, similar calculations were completed for the silicates in Table 1. As the trends between the MSDAs for the SiO bonds and OO separations are the same as those recorded for ordered frameworks, we conclude that the tetrahedra in these silicates also behave as rigid bodies. Therefore, a TLS analysis was completed for each silicate group to obtain an  $L$  tensor, using a Fortran77 program written by us for this purpose. With Equation 2, the thermally corrected coordinates of the atoms for each tetrahedron were estimated, and  $R_{\text{TLS}}(\text{SiO})$  was calculated for each bond.

Using these estimates of the mean SiO bond lengths, expansion rates for  $R_{\text{TLS}}(\text{SiO})$  were calculated and are presented in Table 1, where it is seen that almost all of the bonds expand with increasing temperature. Figure 1 compares the variation with temperature of the apparent  $\text{Si}_{1\text{m}}\text{O}_{\text{bm}}$  bond length in low albite with that of the TLS estimate of the mean bond length. This plot shows that the TLS corrected bond length is appreciably longer, ~0.03 Å, than the apparent length of the bond at 1200 K. As the expansion rates of all the TLS corrected SiO bond lengths in low albite are similar to that of the  $\text{Si}_{1\text{m}}\text{O}_{\text{bm}}$  bond, we may conclude that the SiO bond lengths in low albite expand, as expected, with increasing temperature.

In a study of the high-temperature crystal chemistry of single chain silicates, Cameron et al. (1973) suggested that

TABLE 1. Linear regression slopes ( $\times 10^{-6}$ ) for  $R(\text{SiO})$ ,  $R_{\text{TLS}}(\text{SiO})$ ,  $V(\text{SiO}_4)$ , and  $V_{\text{TLS}}(\text{SiO}_4)$  as a function of temperature (K)

	$R(\text{SiO})$ (Å/K)	$R_{\text{TLS}}(\text{SiO})$ (Å/K)	$V(\text{SiO}_4)$ (Å <sup>3</sup> /K)	$V_{\text{TLS}}(\text{SiO}_4)$ (Å <sup>3</sup> /K)
<b>Albite</b>				
$\text{Si}_{1\text{m}}\text{O}_{\text{a1}}$	-5(1)	13(1)	-17(2)	55(3)
$\text{Si}_{1\text{m}}\text{O}_{\text{bm}}$	-6(1)	15(1)		
$\text{Si}_{1\text{m}}\text{O}_{\text{cm}}$	-3(1)	12(1)		
$\text{Si}_{1\text{m}}\text{O}_{\text{om}}$	-2(1)	15(1)		
$\text{Si}_{2\text{o}}\text{O}_{\text{a2}}$	-7(2)	6(2)	-14(2)	44(1)
$\text{Si}_{2\text{o}}\text{O}_{\text{bo}}$	-10(2)	6(2)		
$\text{Si}_{2\text{o}}\text{O}_{\text{cm}}$	6(1)	21(1)		
$\text{Si}_{2\text{o}}\text{O}_{\text{om}}$	-3(1)	12(1)		
$\text{Si}_{2\text{m}}\text{O}_{\text{a2}}$	2(1)	16(1)	-10(1)	51(2)
$\text{Si}_{2\text{m}}\text{O}_{\text{cm}}$	-2(1)	15(2)		
$\text{Si}_{2\text{m}}\text{O}_{\text{co}}$	-1(1)	13(1)		
$\text{Si}_{2\text{m}}\text{O}_{\text{do}}$	-8(1)	7(1)		
<b>Acmite</b>				
SiO1	5(2)	10(1)	10(2)	38(3)
SiO2	0(1)	9(1)		
SiO3a	5(4)	12(4)		
SiO3b	2(2)	9(2)		
<b>Diopside</b>				
SiO1	0(2)	5(2)	7(4)	37(4)
SiO2	-2(2)	7(2)		
SiO3a	5(3)	13(3)		
SiO3b	3(1)	10(1)		
<b>Jadeite</b>				
SiO1	2(1)	6(2)	7(2)	30(3)
SiO2	2(2)	8(2)		
SiO3a	1(1)	7(1)		
SiO3b	5(2)	10(3)		
<b>Spodumene</b>				
SiO1	6(2)	11(2)	5(4)	41(3)
SiO2	-4(1)	7(1)		
SiO3a	1(1)	11(1)		
SiO3b	2(1)	12(1)		
<b>Sodium fluor-richterite</b>				
Si1O1	-4(2)	0(1)	-11(5)	23(3)
Si1O5	-6(1)	4(2)		
Si1O6	-0(3)	9(3)		
Si1O7	-2(2)	9(1)		
Si2O2	2(4)	7(4)	9(10)	40(9)
Si2O4	-8(4)	2(3)		
Si2O5	9(2)	17(2)		
Si2O6	5(2)	14(2)		
<b>Potassium fluor-richterite</b>				
Si1O1	-1(2)	3(1)	3(1)	33(3)
Si1O5	-4(3)	5(4)		
Si1O6	7.9(2)	15.6(8)		
Si1O7	-2(2)	7(1)		
Si2O2	-7(9)	0(1)	-4(9)	30(9)
Si2O4	-6(2)	5(2)		
Si2O5	9(5)	18(5)		
Si2O6	-1.3(1)	6.8(2)		
<b>Andalusite</b>				
SiO2	1(1)	3(1)	5(4)	26(3)
SiO3	1(2)	9(2)		
SiO4	0.2(4)	6.1(5)		
<b>Kyanite</b>				
Si1O4	1(5)	5(5)	10(1)	26(1)
Si1O5	5(6)	8(6)		
Si1O8	0(1)	4(1)		
Si1O10	3(1)	8(1)		
Si2O1	5(1)	8(2)	16(5)	29(5)
Si2O3	4(1)	7(2)		
Si2O7	4(2)	7(2)		
Si2O9	1(5)	5(6)		

the bridging SiO bond lengths,  $R(\text{SiO}_{\text{br}})$ , in these minerals tend to expand at a faster rate than the nonbridging ones,  $R(\text{SiO}_{\text{nbr}})$ . The data in Table 1 seem to support this claim. For example, the average expansion rate of the bridging

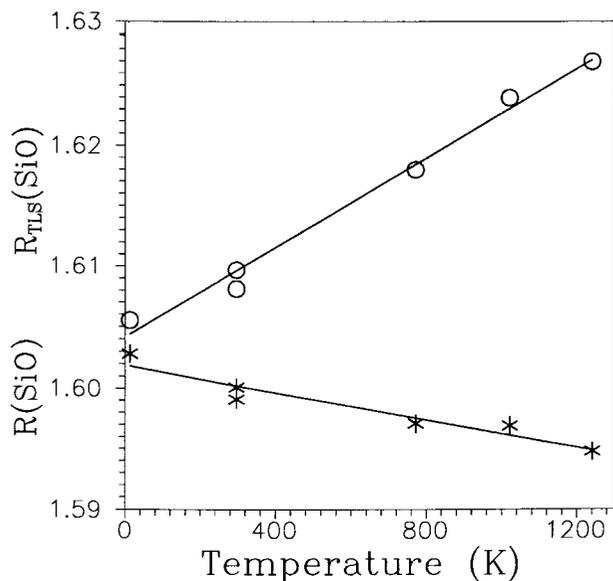


Fig. 1. A scatter diagram of the variation of the SiO bond length with temperature for the  $\text{Si}_{1m}\text{O}_{3m}$  bond in low albite. The uncorrected, apparent bond lengths,  $R(\text{SiO})$ , are plotted as asterisks, and the TLS bond lengths,  $R_{\text{TLS}}(\text{SiO})$ , corrected for rigid-body libration, are plotted as open circles. Note that the uncorrected bond lengths appear to shorten with increasing temperature; however, when corrected, the bonds increase in length.

$\text{SiO}_{\text{br}}$  bonds,  $\langle \partial R_{\text{TLS}}(\text{SiO}_{\text{br}}) / \partial T \rangle$ , for the single chain silicates,  $10.5 \times 10^{-6} \text{ \AA/K}$ , is significantly larger than that,  $7.8 \times 10^{-6} \text{ \AA/K}$ , calculated for  $R_{\text{TLS}}(\text{SiO}_{\text{nbr}})$ . In addition,  $\langle \partial R_{\text{TLS}}(\text{SiO}_{\text{br}}) / \partial T \rangle$  calculated for low albite, which only contains  $\text{O}_{\text{br}}$ , is larger,  $12.6 \times 10^{-6} \text{ \AA/K}$ , than  $\langle \partial R_{\text{TLS}}(\text{SiO}_{\text{nbr}}) / \partial T \rangle$ ,  $6.0 \times 10^{-6} \text{ \AA/K}$ , calculated for andalusite and kyanite, which only contain  $\text{O}_{\text{nbr}}$ . There appear to be two families of expansion rates, with  $R_{\text{TLS}}(\text{SiO}_{\text{br}})$  expanding at nearly twice the rate of  $R_{\text{TLS}}(\text{SiO}_{\text{nbr}})$ .

With the coordinates obtained from the TLS modeling, volumes were calculated for each of the silicate tetrahedra in the nine silicates. In an examination of the variation of these volumes,  $V_{\text{TLS}}$ , with temperature, linear regression analyses were completed for  $V_{\text{TLS}}$  as a function of  $T$ . The resulting expansion rates for these tetrahedra are given in Table 1. The correlations between  $V_{\text{TLS}}$  and  $T$  were found to be better developed than those between  $R_{\text{TLS}}(\text{SiO})$  and  $T$ . The overall average expansion rate of  $V_{\text{TLS}}$  is  $35 \times 10^{-6} \text{ \AA}^3/\text{K}$ , a value that is significantly larger than the zero value reported by Hazen and Finger (1982) and corroborated by our nine silicates for the silicate tetrahedra uncorrected for thermal motion. As observed above,  $R_{\text{TLS}}(\text{SiO}_{\text{br}})$  increases, in general, at a faster rate with increasing temperature than does  $R_{\text{TLS}}(\text{SiO}_{\text{nbr}})$ . Therefore, it is not surprising that the silicate tetrahedra in low albite, where each tetrahedron consists of four  $\text{O}_{\text{br}}$ , expand at about twice the rate as they do in kyanite and andalusite, where each tetrahedron consists of four  $\text{O}_{\text{nbr}}$ . The tetrahedral volumes for the single and double chain silicates, where the tetrahedra contain two or three  $\text{O}_{\text{br}}$ , ex-

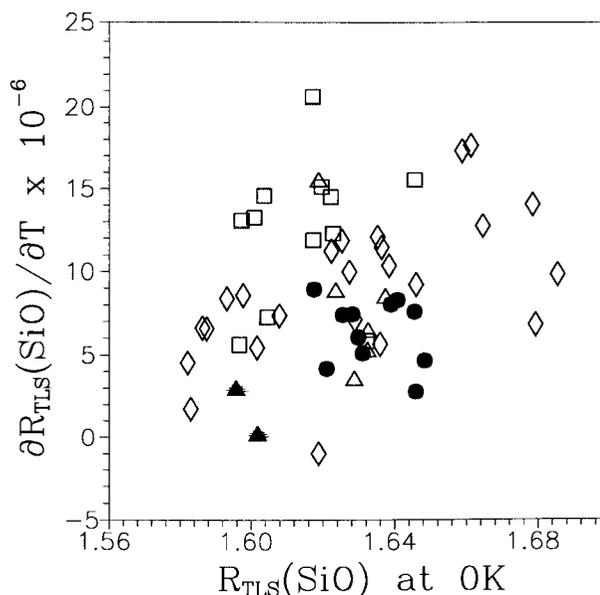


Fig. 2. A scatter diagram of the slope vs. intercept for  $R_{\text{TLS}}(\text{SiO})$ , indicating that the expansion rates of mean SiO bonds do not seem to depend on bond length. The low albite tetrahedral data, with four  $\text{O}_{\text{br}}$ , are plotted as squares, the chain silicates, with three and two  $\text{O}_{\text{br}}$ , are plotted as triangles and diamonds, respectively, and the orthosilicates, with no  $\text{O}_{\text{br}}$ , are plotted as circles. The open symbols indicate bridging bonds, and the closed ones indicate nonbridging bonds. Note that the bridging bonds tend to have larger expansion rates than the nonbridging ones.

pand at an intermediate rate. As in Cameron et al. (1973), no explanation is currently offered of why SiO bridging bonds expand at a faster rate than nonbridging ones.

In a study of the thermal expansion and high-temperature crystal chemistry of the  $\text{Al}_2\text{SiO}_5$  polymorphs, Winter and Ghose (1979) argue that longer bonds should show a greater increase in length with increasing temperature than shorter ones because the latter are usually stronger (see also Megaw, 1971; Hazen and Prewitt, 1977). This argument not only seems to hold for the values of  $R(\text{SiO})$  recorded for these aluminosilicates, but also for silicates in general (Hazen and Finger, 1982). However, Figure 2 shows for the nine silicates studied that the expansion rate of SiO seems to be independent of  $R_{\text{TLS}}(\text{SiO})$ . It also shows that the expansion rate of an SiO bond seems to be related to whether the bond involves a bridging or nonbridging O atom, with bridging bonds tending to expand at faster rates than nonbridging ones. On the other hand, the expansion rates of the tetrahedral volumes seem to depend on  $V_{\text{TLS}}$ , with the volumes of the smaller tetrahedra in low albite increasing at a faster rate than those of the larger tetrahedra in the remaining eight silicates (Fig. 3). As the linkages of the tetrahedra in low albite are different from those in chain silicates and orthosilicates, it appears that the expansion rates also depend on the tetrahedral linkage, with expansion rates increasing with the number of bridging O atoms. This is contrary to

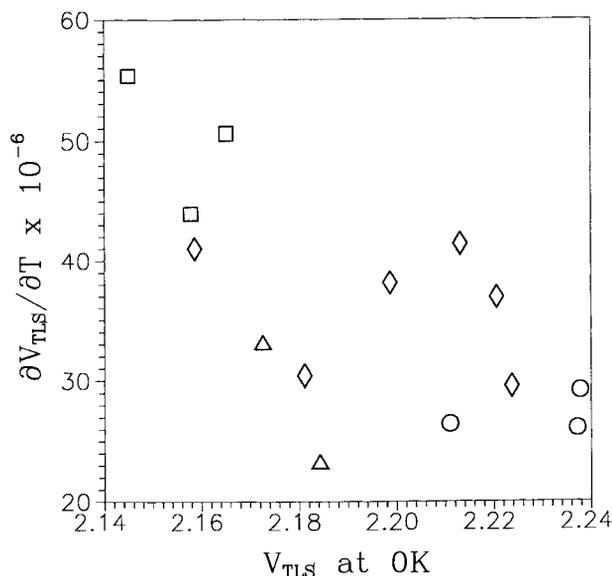


Fig. 3. A scatter diagram of the slope vs. intercept for  $V_{\text{TLS}}(\text{SiO}_4)$ . The low albite tetrahedral data, with four  $\text{O}_{\text{br}}$ , are plotted as squares, the chain silicates, with three and two  $\text{O}_{\text{br}}$ , are plotted as triangles and diamonds, respectively, and the orthosilicates, with no  $\text{O}_{\text{br}}$ , are plotted as circles. The distribution of these data suggests that expansion rate of  $V_{\text{TLS}}$  depends on the magnitude of  $V_{\text{TLS}}$ , which represents the mean volume of the tetrahedra, at 0 K.

the suggestion of Hazen and Finger (1982) that each coordinated polyhedron has a unique volume expansion coefficient.

#### A SIMPLE RIGID BOND MODEL CORRECTION

It is an extensive undertaking to calculate the  $L$  matrix that is required to correct the SiO bond length for thermal motion effects using Equation 2. Consequently, a simpler expression for correcting rigid bond lengths in coordinated polyhedra will be derived that uses the isotropic rather than the anisotropic temperature factors of the atoms that make up the polyhedra. The necessary and sufficient conditions that must hold for this simple rigid bond (SRB) correction are as follows: (1) The bonds must appear rigid, and (2) the coordinated cation must only exhibit translational motion with little or no librational motion.

If the bonds of a coordinated polyhedron,  $XY_n$ , appear to be rigid, then the interatomic separation between the central cation,  $X$ , and each of its coordinated anions,  $Y$ , will tend to remain fixed. This implies that the MSDAs of the  $X$  and  $Y$  atoms will tend to be equal along an  $XY$  bond,  $z_{\text{YX}}^2 = z_{\text{XY}}^2$  (Hirshfeld, 1976; Dunitz et al., 1988). In particular, Downs et al. (1990) have shown that this condition seems to hold for the SiO bonds in a large number of ordered framework silicates. We have studied more than 400 other silicate structures and have found that this condition holds for the SiO bonds in the great majority of these structures.

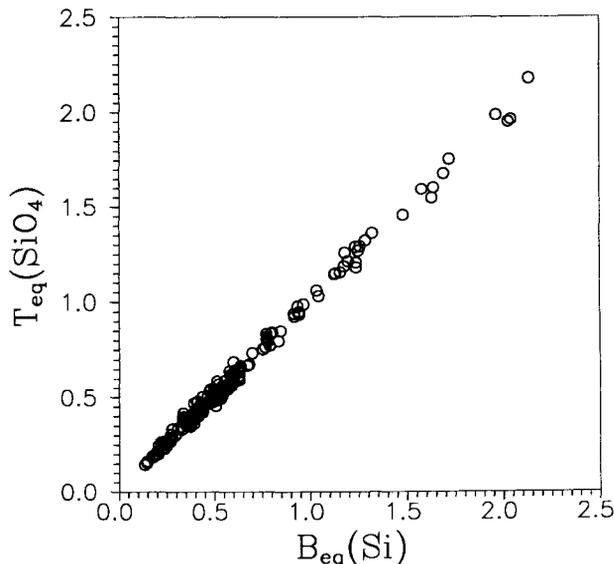


Fig. 4. A scatter diagram of the equivalent isotropic temperature factor for the Si atom,  $B_{\text{eq}}(\text{Si})$ , against the derived equivalent isotropic translational motion parameter,  $T_{\text{eq}}(\text{SiO}_4)$ . The Pearson correlation coefficient is 0.997. This plot indicates that the thermal motion of the Si atom can be considered to be translational only and that there is essentially no librational component to its motion.

If the second condition is satisfied, then the axes of libration of the coordinated polyhedron lie near the central cation. When this is the case, the  $T$  matrix, obtained from the TLS fit, should match the temperature factor matrix of the cation within its experimental errors. All the framework structures examined by Downs et al. (1990) and all the silicates examined in this paper, including the great majority of the other 400 silicate structures mentioned above, exhibit this property. This condition is demonstrated in Figure 4, where the isotropic equivalent of the translational motion of a silicate group,  $T_{\text{eq}}(\text{SiO}_4)$ , is seen to be highly correlated with the isotropic equivalent temperature factor of the central Si atom,  $B_{\text{eq}}(\text{Si})$ . In this case,  $T_{\text{eq}}(\text{SiO}_4)$  is calculated using the same formalism that is used to calculate  $B_{\text{eq}}(\text{Si})$ . Interestingly, the sixfold-coordinated polyhedra in many of these silicates conform with this condition as well.

Suppose that (1) the center of libration of the  $XY_n$  coordinated polyhedron is located at the central  $X$  atom, and (2)  $L_1^2$  and  $L_2^2$  are the MSDAs of the  $Y$  atom, ascribed to its libration, projected onto the axes  $X_1$  and  $X_2$ . In Figure 5, we show a set of Cartesian coordinate axes,  $\{X_1, X_2, X_3\}$ , where  $X_3$  is chosen to be parallel to the  $XY$  bonds in the polyhedron and  $X_1$  and  $X_2$  are chosen to be perpendicular to the bond. The MSDA of libration projected onto a plane perpendicular to the bond is given by  $L_1^2 + L_2^2$ , and so we have

$$R_{\text{SRB}}^2 = R^2 + L_1^2 + L_2^2.$$

If assumption 2 is satisfied, then

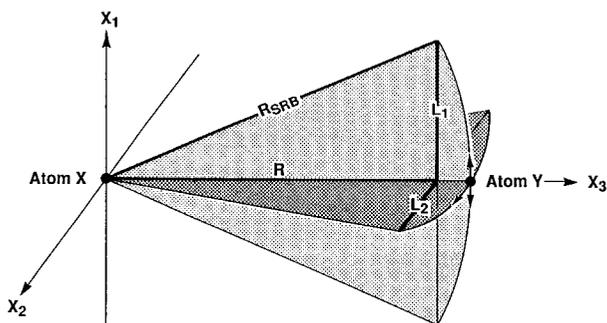


Fig. 5. Librational motion of an  $XY$  bond in a  $XY_n$  rigid coordinated polyhedron, modified after Willis and Pryor (1975).  $R_{\text{SRB}}$  denotes an  $XY$  bond corrected for simple rigid bond motion,  $R$  is the apparent  $XY$  bond length, and  $L_1$  and  $L_2$  denote the root-mean-square displacement amplitude of atom  $Y$  ascribed to the librational motion of the  $XY_n$  coordinated polyhedron projected on a plane perpendicular to  $R$ .

$$L_1^2 + L_2^2 = \sigma_{1,Y}^2 - \sigma_{1,X}^2 + \sigma_{2,Y}^2 - \sigma_{2,X}^2$$

where  $\sigma_{i,X}^2$  and  $\sigma_{i,Y}^2$  are the MSDAs of atoms  $X$  and  $Y$  projected onto the  $X_i$ th axis. If condition 1 is satisfied, i.e.,  $z_{YX}^2 = z_{XY}^2$ , then we have

$$\begin{aligned} R_{\text{SRB}}^2 &= R^2 + (z_{YX}^2 + \sigma_{1,Y}^2 + \sigma_{2,Y}^2) \\ &\quad - (z_{XY}^2 + \sigma_{1,X}^2 + \sigma_{2,X}^2) \\ &= R^2 + \frac{3}{8\pi^2} [B_{\text{eq}}(Y) - B_{\text{eq}}(X)] \end{aligned} \quad (4)$$

where  $B_{\text{eq}}$  is the isotropic equivalent temperature factor. It is noteworthy that when the two conditions hold,  $\overline{w}_Y^2 - \overline{w}_X^2$  must equal  $L_1^2 + L_2^2$ . This implies that the riding model defined by Equation 3 provides a good estimate of the mean bond lengths for rigid coordinated polyhedra.

Boisen et al. (1990) found that  $R(\text{SiO})$  correlates well with  $B(\text{O})-B(\text{Si})$ . This correlation is given a theoretical basis by Equation 4. In fact, it can be shown that the regression coefficient for  $R(\text{SiO})$  vs.  $B(\text{O})$  should be  $\sim 3/(32R\pi^2) = 0.0059$  if it is assumed that  $B(\text{Si}) \sim \frac{1}{2}B(\text{O})$ . The regression coefficient obtained by Boisen et al. (1990) for the silica polymorphs and the clathrasils is  $\sim 0.006$ , matching the theoretical value given above.

The simple rigid bond model, as observed above, indicates that the isotropic temperature factors of the anions making up a rigid coordinated polyhedron should be significantly larger than that of the coordinated cation, regardless of the masses of the atoms, because the temperature factors of the anions embody all of the translational motion of the cation plus the librational motion of the coordinated polyhedron. This observation is supported, for example, by a structural analysis of  $\text{SiS}_2$  (Prewitt and Young, 1965) that shows that the isotropic temperature factors of the S atoms making up the rigid  $\text{SiS}_4$  tetrahedra are significantly larger,  $B_{\text{iso}}(\text{S}) = 1.3 \text{ \AA}^2$ , than those observed for Si,  $B_{\text{iso}}(\text{Si}) = 0.7 \text{ \AA}^2$ , despite the

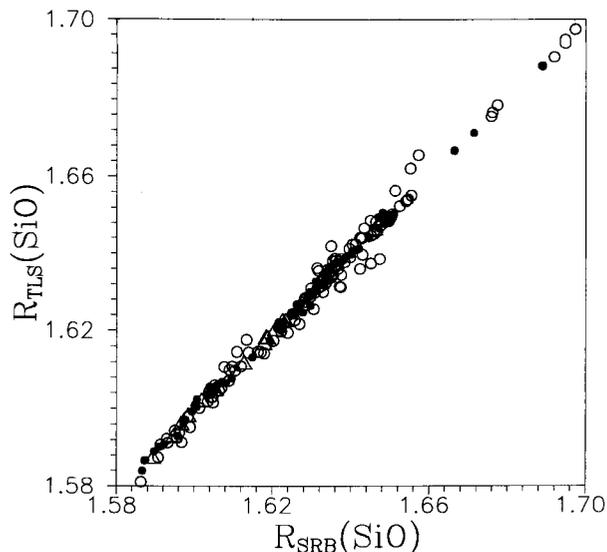


Fig. 6. A scatter diagram of  $R_{\text{SRB}}(\text{SiO})$  vs.  $R_{\text{TLS}}(\text{SiO})$ . The Pearson correlation coefficient is 99.6%, with 86% of the SRB corrected bond lengths being within  $0.002 \text{ \AA}$  of the TLS corrected bond lengths. Open triangles represent bond length data recorded at low temperature, solid circles represent data recorded at room temperature, and open circles represent data recorded at high temperatures.

fact that the mass of a S atom is about 15% larger than that of Si. A similar observation can be made for the rigid  $\text{SiSe}_4$  tetrahedra in  $\text{SiSe}_2$ : the  $B_{\text{iso}}$  value for Se ( $2.7 \text{ \AA}^2$ ) is observed to be significantly larger than the  $B_{\text{iso}}$  value observed for Si ( $2.1 \text{ \AA}^2$ ) (Peters and Krebs, 1982), despite the larger mass of Se. If the temperature factors of these anions were smaller than that of Si, then Equation 4 would predict that the corrected bond length would be shorter than observed, which contradicts Busing and Levy's assertion that thermally corrected bond lengths must always be longer than uncorrected ones. If the predictions of this model are correct, then a refined structure may be viewed as suspect and unsuitable for a crystal chemical study of bond length and angle variations (Boisen et al., 1990) when the  $B$  values of a cation in a rigid coordinated polyhedron are significantly larger than the  $B$  values of the coordinating anions.

As shown in Figure 6,  $R_{\text{SRB}}(\text{SiO})$  is highly correlated with  $R_{\text{TLS}}(\text{SiO})$ , with a Pearson correlation of 0.996 and a slope and intercept of 1.0 and 0.0, respectively. More than 210 of the 244 SRB corrected bond lengths agree to within  $0.002 \text{ \AA}$  of the TLS corrected values. The ones that depart from the regression line were recorded in high-temperature structural analyses, where the rigid model may break down and  $\text{OSiO}$  angle bending modes may be activated (Megaw, 1973). Figure 6 demonstrates that the simple rigid bond correction is a good estimator of the mean bond lengths for a coordinated polyhedron exhibiting rigid bond motion. The expansion rates of both the bond lengths and the tetrahedral volumes provided by

the SRB corrections are statistically identical with those provided by a TLS correction.

### CONCLUSIONS

A TLS analysis was completed in this study on the silicate tetrahedra in nine silicates whose structures were determined over a range of temperatures from 15 to 1250 K. The analysis yields bond lengths for the silicate structures determined at room temperature that are slightly longer ( $\sim 0.005$  Å) than the uncorrected ones. On the other hand, the analysis yields bond length data for the structures determined at high temperatures that exceed the uncorrected bond lengths by as much as 0.03 Å. The libration angles calculated for the silicates examined in this study were all less than 12°. Our analysis of the systematic errors due to the correction of bond lengths by the TLS method indicates that the maximum error in the resulting bond lengths is no more than  $\sim 0.001$  Å, which is well within the estimated error. Furthermore, we have found that corrected bond lengths almost always increase in a regular way with increasing temperature.

### ACKNOWLEDGMENTS

The National Science Foundation is thanked for supporting this work with grant EAR-8803933, and Sharon Chiang is thanked for drafting Figure 5. Maryellen Cameron provided helpful insight into the experimental pitfalls of obtaining and refining high-temperature diffraction data. C. Williams of the Virginia Tech Physics Department enjoys our debt of gratitude for his guidance in the theory of lattice vibrations. We thank an anonymous reviewer for his constructive suggestions.

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MANUSCRIPT RECEIVED SEPTEMBER 3, 1991

MANUSCRIPT ACCEPTED MARCH 9, 1992