Phys Chem Minerals (1988) 15:409–415

PHYSICS AND CHEMISTRY OF MINERALS

Resonance Bond Numbers: A Graph-Theoretic Study of Bond Length Variations in Silicate Crystals

M.B. Boisen, Jr.[1], G.V. Gibbs[2], and Z.G. Zhang[3]

[1] Department of Mathematics, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA
[2] Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA
[3] Department of Mathematics and Physics, Chengdu College of Geology, Changdu 610059, Sechuan, People's Republic of China

Abstract. The resonance bond number n, as defined in this paper, is designed to describe the strength of an XO bond as a function of the kinds of atoms present and which atoms are bonded. The calculation of n is made on a fragment extracted from the crystal encompassing the XO bond. If this fragment consists of only the X atom and its coordinating O atoms, then n is numerically equal to the Pauling bond strength, s. In this study a graph-theoretic algorithm is developed permitting the calculation of n using fragments including up to 50 atoms. This algorithm was used to calculate n for all of the bonds in ten silicate crystals. Since bond strength is be inversely related to bond length, we examined the relationship between these two variables and found that n can be used to explain over 70 percent of the variation of XO bond lengths from their average values in the crystals.

A fit of the parameter n/r, where r is the row number in the periodic table of the metal atom X, to the observed bond lengths in these crystals yielded the equation $R(XO)=1.39(n/r)^{-0.22}$ which explains over 95.5 percent of the variation of bond lengths in the crystals. The fact that the same formula with s replacing n was found in an earlier study to be a good estimator of average bond lengths in crystals shows that n relates to individual variations in bond lengths in crystals in the same way that s relates to average bond lengths in crystals.

Using minimum energy SiO, AlO and MgO bond lengths and harmonic force constant data calculated for these bonds in hydroxyacid molecules, theoretical equations similar to those used by Pauling to explain bond length variations in hydrocarbons are derived. Bond lengths calculated with these equations for the 10 crystals shows that 95 percent of the variation of the observed bond lengths in these crystals can be explained in terms of n by this purely theoretical model.

Introduction

The extent to which the stereochemistry of a crystal can be recovered from a knowledge of the connectivity and the number of valence electrons on each of its constituent atoms has been studied by numerous researchers. In a study of the principles governing the structures of complex ionic crystals, Pauling (1929) defined the electrostatic strength, s, of a bond in such crystals to be z/v where z is the ionic valence of the cation and v is the coordination number of the cation. With this definition, he was able to explain the connectivity of such crystals by observing that the sum of the bond strengths reaching each anion in the structure equaled the ionic valence of the anion with the sign changed. In a study of bond length variations in oxides, Baur (1970) has since found that the sum of the bond strengths, denoted p_0, received by the oxide ion can deviate up to about 40 percent from a value of 2.0. He also found that the individual XO bond lengths are linearly correlated with shorter bonds involving smaller p_0-values. Using the slopes of the regression lines fit to the observed data, he was able to modify average observed XO bond lengths to reproduce XO bond length variations in crystals to within about 0.01 Å. This approach has the drawback of being dependent on empirical information. However, Gibbs et al. (1981) and Geisinger et al. (1985) have completed non-enpirical MO calculations on hydroxyacid silicate and aluminosilicate molecules and have reproduced the observed XO bond length, $X=$Si, Al, versus p_0 curves found for silicate and aluminosilicate crystals.

For aromatic hydrocarbons, Pauling and Brockway (1937) devised a method of estimating CC bond lengths in molecules by mixing the potential energy curves for single bonds (with bond number, $n=1$) and for double bonds ($n=2$) to obtain a potential energy function for all intermediate values of n (See Footnote 3, Pauling et al. 1935). Bond length estimates are then found by taking the derivative of this potential energy function with respect to the bond length and setting it equal to zero. Estimates obtained in this manner, assuming a ratio of single to double bond force constants of 1.84 and using bond numbers calculated for Kekulé-type resonance structures in which a particular bond is double, gave bond lengths that reproduced those in several sterically-unhindered molecules to within about 0.01 Å (Cruickshank 1962). In 1952, Pauling extended the method to XO_4 tetrahedral groups ($X=$Si, P, S, Cl) by assuming that if the electron pairs resonate among allowable positions with the valence (i.e. the number of electrons involved in forming bonds) of the metal atoms divided equally among these positions, then the valence of the oxygen atoms would tend to be satisfied (see footnote 64, p. 547; Pauling 1960). This sharing of electron pairs to complete the stable ten-electron configuration of Ne for the oxygen atom in a covalent crystal is equivalent to the rule that the sum of the electrostatic bond strengths reaching the oxide ion (with the Ne configuration) in an ionic crystal is 2.0. By constructing the resonating Lewis structures for the XO_4 groups as a function of bond number, he was able to estimate mean XO bond lengths in crystals to within 0.01 Å.

Fundamental to these methods for estimating XO bond length variations in crystals is the definition and calculation of bond numbers. We will base our definition on resonance structures, and so we will refer to them as resonance bond numbers and denote them by n. The technique for calculating the resonance bond numbers will be discussed in general in the next two sections. Because of the computational effort involved, the size of such a fragment was limited to include no more than 50 atoms. This is the severest limitation in the execution of the model. The model itself has some theoretical limitations in that the definition of n ignores steric hindrances, nonbonded and bonded repulsions and treats all bonds as purely covalent. We investigate whether the values of n calculated in this manner are reasonable by demonstrating the degree to which n describes the variation of bond lengths from their mean values in 10 silicate crystals. We find that n can be used to explain over 70 percent of the bond length variation in these crystals not explained by the average values of each type of XO bond.

We explore two methods of using n to estimate bond lengths in crystals. In the first, we follow the approach given by Gibbs et al. (1987b) and fit the parameter n/r to the observed bond lengths in the crystals obtaining a bond length estimator that is the result of both empirical and theoretical data (r is the row number in the periodic table of the X cation). We will find that the resulting equation explains over 95.5 percent of the variation in bond lengths in the crystals studied. The second method is entirely theoretical using quadratic force constants and bond lengths obtained in *ab initio* molecular orbital (MO) calculations together with specific bond numbers to construct potential energy functions in a manner similar to that used by Pauling and Brockway (1937).

Until recently, the second method would not have been feasible because of the difficulty in obtaining reliable values using *ab initio* methods. In the last few years, with the development of sophisicated quantum mechanical programs and high-speed computers, a large number of calculations have been completed on a variety of molecules (Hehre et al. 1986). Such calculations on hydroxyacid molecules have, for example, been used to model bond length and angle variations in a variety of chemically similar crystals. When sufficiently robust basis sets are used, the resulting lengths and angles reproduce average values found in crystals fairly well (Gibbs et al. 1987b and references therein). Since credible Hartree-Fock calculations are more difficult to make for the transition metal ions, we only apply the non-empirical method to XO bonds where $X=$ Si, Al and Mg. While the MO calculations account for the local environment of these XO bonds, the resonance bond numbers will incorporate information about the global environment of the bond. We will see that this method can be used to explain 95 percent of the bond length variation in the crystals studied.

Resonance Bond Numbers and Bond Length Variations in Crystals

In this study we consider representative fragments taken from the monosilicate andalusite, from several monopolysilicates including diopside, jadeite, acmite, spodumene, $NaInSi_2O_6$ and $NaCrSi_2O_6$, from the dipolysilicates fluorotremolite and sillimanite and from the tektosilicate cordierite. Each fragment is centered on a given X cation and is used to find the resonance bond numbers for the XO bonds associated with this central X atom. The chosen fragment is then modeled by a graph that we will refer to as the pattern graph. By a graph, we mean a set of vertices and a set of edges such that each edge joins two distinct vertices called the endpoints of the edge. An edge is said to be incident to each of the two vertices that it joins. The edges have no direction defined on them and any two vertices may be joined by several distinct edges (cf. Bondy and Murty 1976). The pattern graph is constructed so that each vertex represents an atom and each edge represents a bond in the fragment. That is, an edge joining two vertices exists in the pattern graph if and only if the atoms represented by these vertices are bonded in the fragment. When constructing this graph, some decisions must be made as to how to handle those atoms in the fragment whose coordination spheres do not lie completely in the fragment. These atoms will always be the furthest atoms in the fragment from the central X cation. A premise suggested by recent results in the molecular modeling of crystals, is that the further an atom is from the XO bond under study, the less it influences the bond. This suggests that one may simplify the model of the portion of the fragment involving these atoms without seriously affecting the final values of the resonance bond numbers. Because of this simplification, we were able to include these atoms in the calculation without incurring excessive computational effort. This method is demonstrated in detail in the next section of the paper for the case of andalusite.

After the pattern graph is established, all graphs are found that relate to the set of all possible Lewis structures for the fragment. Such a graph will be called a Lewis graph. The set of vertices for a Lewis graph based on a given pattern graph is the same as the set of vertices in the pattern graph and these vertices are interpreted in the same manner (as representing atoms in the fragment). However, unlike in the pattern graph, an edge in a Lewis graph represents a pair of shared electrons between the atoms corresponding to the vertices. Since such shared electrons are assumed to occur only along bonds, an edge can exist in a Lewis graph only if the corresponding vertices are joined in the pattern graph. In a Lewis structure, the number of pairs of shared electrons corresponding to a given atom equals the valence of that atom. Consequently, we require that the number of edges incident to a given vertex in a Lewis graph equals the valence of the atom represented by the vertex when the coordination sphere of that atom is completely contained in the fragment. When the coordination sphere is not contained in the fragment, it could form electron pairs with atoms outside the fragment and so we relax this condition and insist only that the number of edges incident with the corresponding vertex be less than or equal to the valence of the atom. The number of edges incident with a given vertex is called the degree of the vertex. Hence we define a graph G to be a Lewis graph associated with a given pattern graph if and only if

(1) the set of vertices of G is the same as that of the pattern graph,

(2) the only vertices that are joined by edges in G are those joined in the pattern graph, and

(3) the degree of each vertex of G that corresponds to an atom whose coordination sphere is completely contained

in the fragment equals the valence of that atom. The degree of each of the remaining vertices must be less than or equal to the valence of its corresponding atom.

The resonance bond number, n, of each XO bond in the fragment that involves the central X cation is defined to be the average number of edges (electron pairs) that join the vertices corresponding to X and O averaged over all Lewis graphs associated with the pattern graph used to model the fragment. More details of how the resonance bond numbers are calculated will be discussed in the next section. In this section, we explore how the resonance bond numbers may be used to describe bond length variations in the crystals from which the fragments have been extracted. We calculated resonance bond numbers, n, for all of the bonds in the ten crystals used in this study including those involving such transition metal atoms as Fe, In, Cr, Sc and Mn.

If the resonance bond numbers, n, faithfully reflect the underlying theretical principles, then the variation of an observed XO bond length from its average value in the ten crystals, $\langle R_0(XO)\rangle$, should be related inversely to the variation of the corresponding resonance bond number from its average value. To test whether this is the case, we found $\langle R_0(XO)\rangle$, for each of the XO bonds with a given coordination number that appears in the crystals (the average taken over the different bond lengths that occur in these specific crystals). Since the average resonance bond number for the XO bonds is $\langle n\rangle = Z/v$ where Z is the valence of the cation and v is the coordination number (note that $\langle n\rangle$ is numerically equal to the electrostatic strength of a bond), we expect an inverse relationship between the ratio $\langle R_0(XO)\rangle / R_0(XO)$ and the ratio $\langle n\rangle/n$. Since these ratios are both one when n and $R_0(XO)$ are at their average values, for $\langle n\rangle/n$ to estimate $\langle R_0(XO)\rangle/R_0(XO)$, the only scaling that will be necessary is to find the best values of t such that

$$\frac{R_0(XO)}{\langle R_0(XO)\rangle} = \left(\frac{\langle n\rangle}{n}\right)^t$$

is as nearly true in the sense of least squares as possible. The best values of t were found to be 0.072 when the X cation is in the second row of the periodic table and 0.342 when it is in the third row. Using this relationship to give the estimate $R(XO)$ to $R_0(XO)$ defined by

$$R(XO) = \langle R_0(XO)\rangle \left(\frac{\langle n\rangle}{n}\right)^t \tag{1}$$

we found that 98.8 percent of the variation in $R_0(XO)$ can be explained in terms of a linear dependence on $R(XO)$. An analysis of $R_0(XO)$ vs. $\langle R_0(XO)\rangle$ shows that 95.5 percent of the variation in $R_0(XO)$ can be explained in terms of a linear dependence on $\langle R_0(XO)\rangle$. Consequently, n provides an explanation of over 70 percent of the variation of $R_0(XO)$ not explained by $\langle R_0(XO)\rangle$. Given that our theoretical basis for n treats the bonds as if they were entirely covalent and ignores any of the ionic aspects of the bonds, we are encouraged by this result.

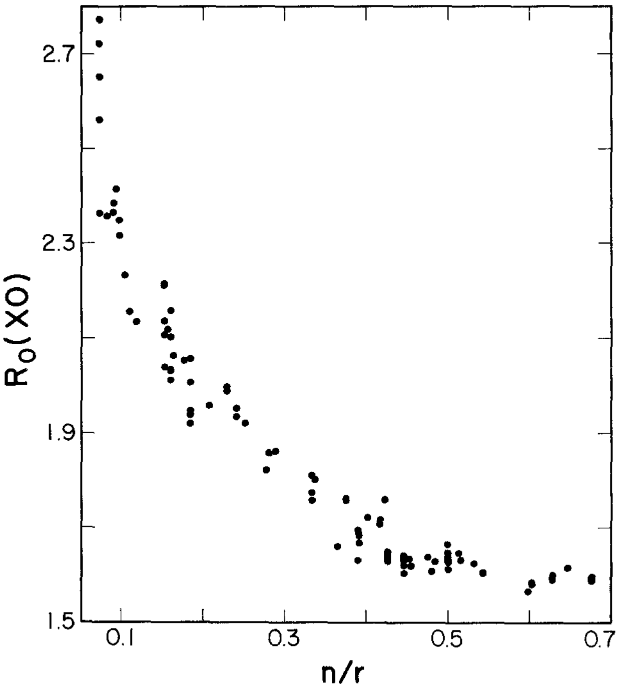

Fig. 1. A plot of $R_0(XO)$ vs. (n/r) where $R_0(XO)$ represents each of the XO bond lengths in 10 silicate crystals, n is the resonance bond number and r is the number of the row in the periodic table of the metal atom X

The analysis leading to equation (1) involved the term $\langle n\rangle/n$ which emphasizes the variation of n from its mean value and ignores the degree to which n can be used to explain variations in bond lengths from one cation to another and from one coordination number to another. We will investigate this issue by adapting the approach taken in Gibbs et al. (1987b). In an attempt to extend a formula relating XO bond lengths to bond strengths for the X cations in the first two rows of the periodic table to the main group cations in the remaining rows, they used the bond strength parameter $p = s/r$ where r is the row number and s is the Pauling bond strength. A least-squares analysis of the functional relationship between the minimum energy bond length data for hydroxyacid molecules calculated by molecular orbital methods and p yielded the formula

$$R(XO) = 1.39\,p^{-0.22} \tag{2}$$

for XO bonds involving first and second row X cations. When this equation was extended to estimate XO bond lengths for X main-group cations for all 6 rows of the periodic table, the resulting estimates served to rank the average values, $R_s(XO)$, reported by Shannon (1976) explaining more than 97 percent of the variation. Following this approach we will explore how well n/r serves to rank the bond lengths in the ten crystals. A graph of (n/r) vs. $R_0(XO)$ (Fig. 1) shows that the bond lengths tend to fall on a single smooth curve similar to the p vs. $R_s(XO)$ plot (see Fig. 3, Gibbs et al. (1987b)). A statistical analysis of these data shows that the function of the form $a(n/r)^b$ that best fits the data displayed in Figure 1 is

$$R(XO) = 1.39\,(n/r)^{-0.22} \tag{3}$$

which, surprisingly, has the same constants as equation (2). Equation (3) explains 95.5 percent of the bond length variations while equation (2) explains 93.4 percent of the variation when each is applied to the 10 crystals. The slope and intercept of the $R(XO)$ vs. $R_0(XO)$ regression line are statistically identical to 1 and 0, respectively.

Table 1. Bond number, n, and minimum energy bond lengths, $R(n)$, and force constants, $f(n)$, for selected hydroxyacid molecules

Molecule	n	$R(n)$ Å	$f(n)$ a.u./Å^2
H_8SiO_6	2/3	1.759	1.96
H_4SiO_4	1	1.626	3.07
H_2SiO_3	2	1.479	4.93
H_9AlO_6	1/2	1.889	1.21
H_5AlO_4	3/4	1.759	1.71
$H_{10}MgO_6$	1/3	2.038	0.68
H_6MgO_4	1/2	1.945	0.86

The analyses employed thus far utilize empirical information. We now consider a completely non-empirical model using bond lengths and force constants obtained from *ab initio* MO calculations. Because it is impractical to carry out such calculations for the transition metal ions, we restrict our attention to calculations for molecules containing Si, Al, Mg, O and H. To model the relationship between resonance bond numbers and bond lengths, we performed calculations on a series of specific molecules (Table 1). In the cases of H_4SiO_4 and H_2SiO_3, we calculated the resonance bond numbers by treating the whole molecule in the same manner as was done for the fragments of the crystals considered above. For the remaining molecules in the table, we took the value of the Pauling bond strength to represent the bond number. The SiO bond length (1.626 Å) associated with a bond number of 1 was obtained by optimizing H_4SiO_4 using a robust 6–31G** basis (Gibbs et al. 1987a). The force constant 3.07 a.u./Å^2 of the bond was then found by applying the forward finite difference method on the analytic gradient. An optimization of the molecule $O{=}Si(OH)_2$ gave a bond length of 1.479 Å associated with a bond number of 2 and a force constant of 4.93 a.u./Å^2. Since the average bond number of an SiO bond in an octahedral SiO_6 group is 4/6 which is not an intermediate value between 1 (for a single bond) and 2 (for a double bond), we used the optimized SiO bond length (1.759 Å) and a force constant 1.96 a.u./Å^2 calculated for H_8SiO_6 (Gibbs et al. 1987b) to provide the necessary information for bond numbers less than 1. The molecules used to obtain bond number information about SiO, AlO and MgO bonds are listed in Table 1 along with the corresponding bond lengths $R(n)$ and force constants $f(n)$. The geometries of the molecules containing MgO and AlO bonds were optimized using 6–31G* bases on Al and Mg, a 6–31G basis on O and an STO-3G basis on H. Again the force constants of the AlO and MgO bonds were determined by a finite difference calculation on the gradient.

Each bond type and bond number given in Table 1 gives rise to a quadratic approximation to the potential $V(n, R)$:

$$V(n,R)=f(n)(R-R(n))^2.$$

Since we do not have sufficient knowledge of the functions $f(n)$ and $R(n)$, except at the specific values of n (shown in Table 1), we combine the special cases of the function $V(n, R)$ to obtain a reasonable functional expression for it. In the case of the SiO bond, we obtain three special cases of $V(n, R)$ corresponding to the bond numbers 2/3, 1 and 2 as shown below:

$$\begin{aligned} V(2/3,R)&=1.96(R-1.759)^2\\ V(1,R)&=3.07(R-1.626)^2\\ V(2,R)&=4.93(R-1.479)^2. \end{aligned}$$

The simplest form for $V(n, R)$ that fits these cases is

$$V(n,R)=c(2/3,n)\,V(2/3,R)+c(1,n)\,V(1,R)+c(2,n)\,V(2,R)$$

where

$$\begin{aligned} c(2/3,n)&=\frac{(n-1)(n-2)}{(2/3-1)(2/3-2)}\\ c(1,n)&=\frac{(n-2/3)(n-2)}{(1-2/3)(1-2)}\\ c(2,n)&=\frac{(n-2/3)(n-1)}{(2-2/3)(2-1)}. \end{aligned}$$

By taking the derivative of $V(n, R)$ with respect to R, we find that the value of R at the minimum of $V(n, R)$, denoted $R(\mathrm{SiO}, n)$, occurs at

$$R(\mathrm{SiO},n)=\frac{f(2/3)\,c(2/3,n)\,R(2/3)+f(1)\,c(1,n)\,R(1)+f(2)c(2,n)\,R(2)}{f(2/3)\,c\,(2/3,n)+f(1)\,c(1,n)+f(2)\,c(2,n)}. \tag{4}$$

Since $R(\mathrm{SiO}, n)$ corresponds to a minimum energy configuration, we expect that $R(\mathrm{SiO})$ should model the SiO bond lengths found in a crystal as a function of bond number n.

In the case of the AlO bond, the *ab initio* calculations provide information at the two values $n=3/4$ and $n=1/2$ (see Table 1). Using the same analysis as discussed above (also see Pauling, 1959), we obtain

$$R(\mathrm{AlO},n)=\frac{f(1/2)\,c(1/2,n)\,R(1/2)+f(3/4)\,c(3/4,n)\,R(3/4)}{f(1/2)\,c(1/2,n)+f(3/4)\,c\,(3/4,n)} \tag{5}$$

where

$$\begin{aligned} c(1/2,n)&=\frac{(n-3/4)}{(1/2-3/4)}\\ c(3/4,n)&=\frac{(n-1/2)}{(3/4-1/2)}. \end{aligned}$$

Curves representing the functions given by equations (4) and (5) are plotted in Figure 2. We have superimposed on these curves the observed bond lengths vs. the resonance bond numbers found using the graph-theoretical approach discussed above. The fact that the curves pass through the observed data as well as they do implies that this approach is reasonable. In Figure 3, $R(X\mathrm{O}, n)$ is plotted against $R_0(X\mathrm{O})$ for each XO bond in the ten crystals where $X=$ Si, Al and Mg. The force constants and bond lengths used to formulate $R(\mathrm{MgO}, n)$ are given in Table 1. A regression analysis of $R(X\mathrm{O}, n)$ vs. $R_0(X\mathrm{O})$ for the combined data for $X=$ Si, Al and Mg shows that 95 percent of the variation in $R_0(X\mathrm{O})$ can be explained in terms of a linear dependence on $R(X\mathrm{O}, n)$.

The Calculation of Resonance Bond Numbers

We will illustrate the method by constructing a graph of a fragment centered on an $X=$ Si atom in the andalusite

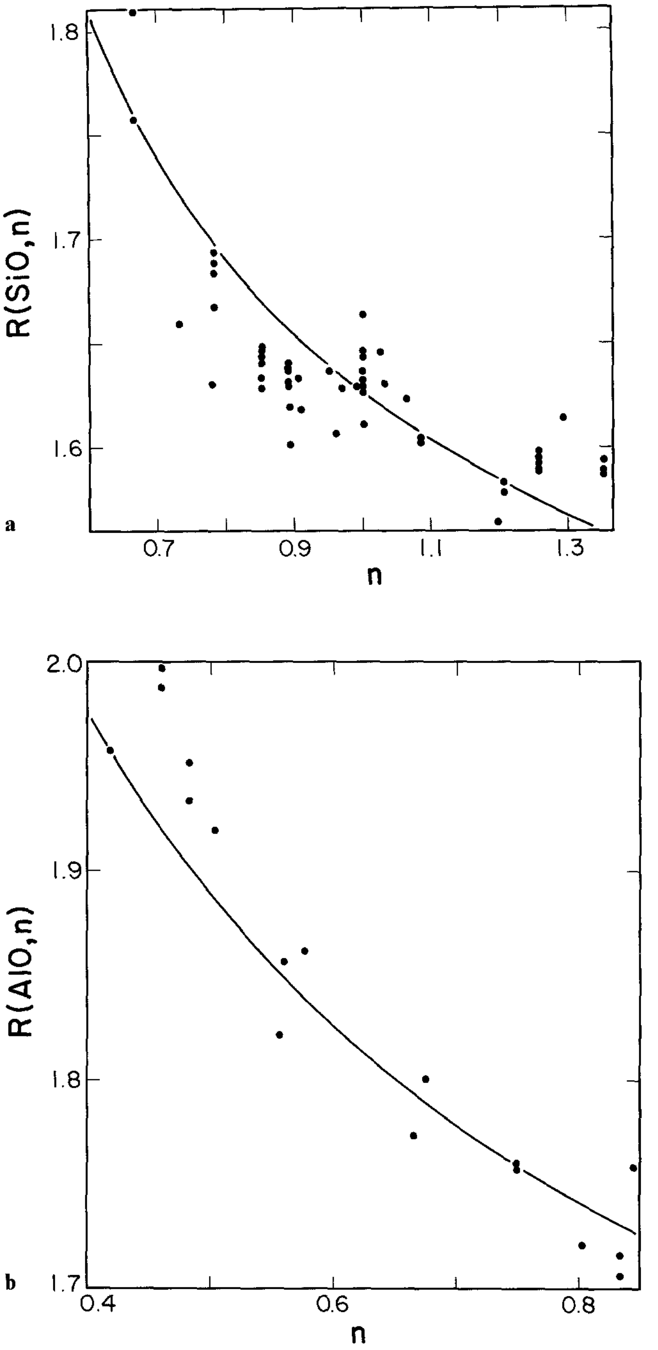

Fig. 2a, b. Curves of $R(XO, n)$ vs. n for (**a**) $X = \mathrm{Si}$ and (**b**) $X = \mathrm{Al}$ defined by formulas (1) and (2), respectively. The bullets represent the observed bond lengths vs. resonance bond numbers for (**a**) the SiO bonds and (**b**) the AlO bonds taken from ten silicate crystals

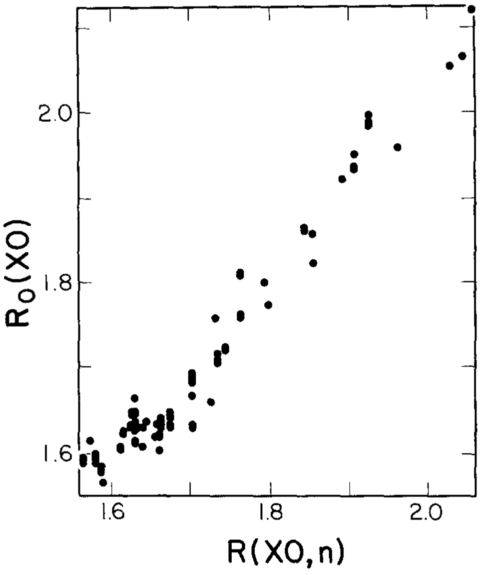

Fig. 3. A plot of $R_0(XO)$ vs. $R(XO, n)$ where $X = \mathrm{Si}$, Al, Mg and the XO bonds are taken from ten silicate crystals. $R_0(XO)$ is defined in Figure 1 and $R(XO, n)$ represents the value calculated using the resonance bond number n for each of these bonds and the appropriate formula $R(\mathrm{SiO}, n)$, $R(\mathrm{AlO}, n)$, or $R(\mathrm{MgO}, n)$

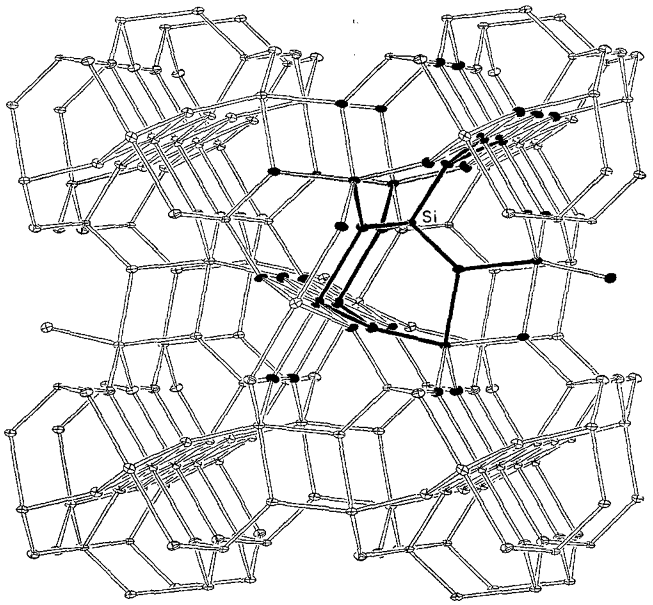

Fig. 4. An ORTEP drawing of the crystal structure of andalusite, Al_2SiO_5 showing the fragment centered of Si to be extracted for our study. The atoms chosen to be in the fragment and the bonds between atoms whose coordination spheres are contained in the fragment are darkened

structure, Al_2SiO_5 (Fig. 4). All of the atoms that will be included in the fragment are darkened in the figure. Note that we have included all atoms that can be reached from the Si atom by passing over three or fewer edges. The pattern graph of this fragment is depicted in Figure 5 where an edge is drawn between each pair of vertices that represent atoms that are bonded in the structure. Among the O atoms that lie a distance of three from the Si atom (that is, can be reached from the Si atom by passing over three bonds and no fewer), one is bonded to three of the Al atoms in the fragment. The connectivity of this atom appears in the graph. Some of the O atoms that are at a distance of three from Si are bonded to two of the Al atoms in the fragment. Because of the computational effort required and the belief that this simplification would have little impact on the final results, these connectivities were ignored and so each of these O atoms are shown twice in the graph, once with each Al atom to which it is bonded.

Two Lewis graphs derived from the pattern graph shown in Figure 5 are shown in Figure 6. Note that each

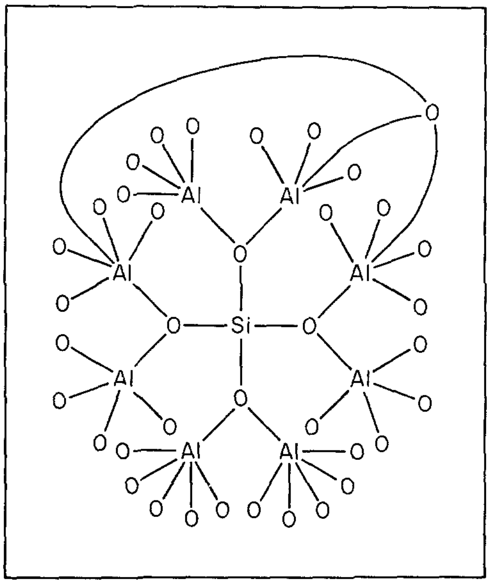

Fig. 5. A graph of a fragment of andalusite centered on an Si atom where each vertex is designated by the atomic symbol of the atom that it represents. This graph serves as a pattern graph in the process of finding the Lewis graphs for this fragment

edge in these graphs corresponds to an edge in the pattern graph but that there are sometimes two edges between a given pair of vertices (representing a double bond), sometimes one (representing a single bond) and sometimes none (representing no bond). There are never more than two edges between a pair of vertices since each edge is incident with a vertex of degree 2 (representing an O atom). Note that the vertices representing Si have degree 4 and those representing Al have degree 3. Therefore, the charges on each of these atoms is zero and so the bonding is modeled as purely covalent.

When searching for all of the Lewis graphs derived from the pattern graph in Figure 5, some organization must be employed because of the large number of combinations that occur based on this pattern graph. For example, since each edge in the pattern graph can result in 0, 1 or 2 edges in a given member of the family, there are $3^{47} = 2.66 \times 10^{22}$ combinations for the placement of these edges and among these there are approximately 83 million Lewis graphs! We searched for these graphs by restating the problem as a system of linear equations in which each equation corresponds to an atom and the unknowns correspond to bonds. For example, if the fourth atom is four coordinate with a valence of 3 and if the 3rd, 5th, 8th and 12th bonds are incident with it, then the fourth equation would look like

$$x_3 + x_5 + x_8 + x_{12} = 3$$

and we would then accept, for this particular equation, any solution consisting of the integers 0, 1 or 2. For the vertices associated with atoms having coordinating atoms outside of the fragment, inequalities were used since we only have an upperbound on the degree of the vertex. Any set of integer values for the variables x_i that satisfies all of the equations and inequalities simultaneously corresponds to a Lewis graph. The average of the x_i values over all of the Lewis graphs is the resonance bond number n for the i^{th} bond. However, the only values of n that we will use from a given fragment are those that are associated with XO bonds that are incident with the central X cation.

To shorten the process for finding all of the integral solutions to our system of equations, we placed the coefficients of these equations into a matrix. We then made our search more efficient by row reducing the matrix taking care to keep integer entries. In all cases, we were able to eliminate as many variables as there were equations. The job of finding the set of all solutions in this reduced matrix was made even more efficient by cutting off branches in the logical search tree that could not be fruitful as early as possible. This was accomplished by a forward checking algorithm that detected when an early choice of the value for one variable made it impossible to accomodate some later variable.

Discussion

In this study, we have shown that the bond lengths in ten silicates can be ranked fairly well in terms of resonance bond numbers calculated for representative fragments of each crystal, using a graph-theoretic model. In this model

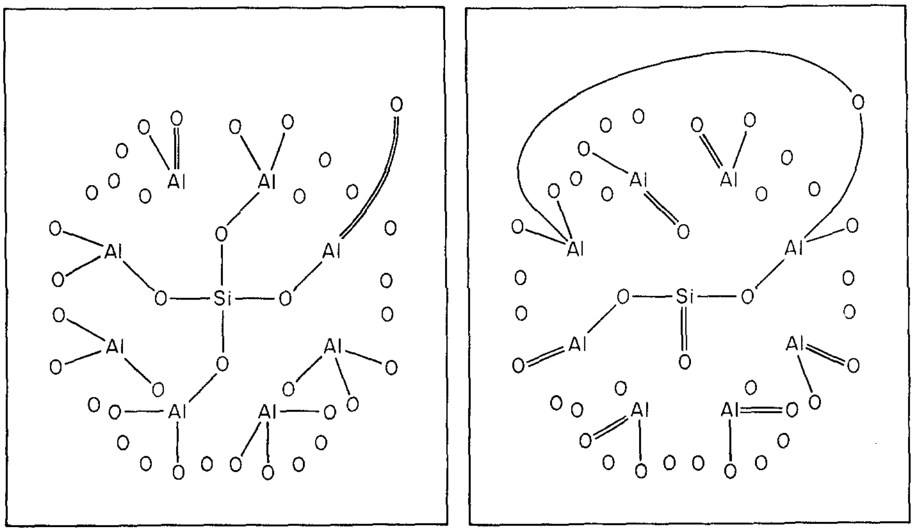

Fig. 6. Two Lewis graphs based on the pattern graph shown in Figure 5. Once all such graphs are found, the resonance bond number is calculated by finding the average number of edges for each SiO bond

it is assumed that the bonding is purely convalent with the sum of electrons in the bonds associated with each atom conferring a neutral inert gas electronic configuration on that atom. From this result one might conclude that the bonding in these silicates is primarily covalent, but this would be unjustified just as it would be unjustified to conclude that the bonding in a silicate is primarily ionic as argued by Zoltai and Stout (1984) simply because Pauling's rules are obeyed. Also, the conclusion by Zoltai and Stout (1984) that the SiO bond behaves as if it is ionic because the length of the bond in a silicate is reproduced by the radius sum of the Shannon and Prewitt (1969) radii is also unjustified in that the radii of both Si^{+4} and O^{-2} were determined in such a manner so as to guarantee that their radius sum equals the average SiO bond length in a silicate.

In conclusion, a variety of bonding models has been proposed that provide an assortment of parameters such as bond strength, bond strength sums, $(d-p)\pi$-bond order, fraction of *s*-character and Mulliken bond overlap populations that rank bond lengths. But as observed by Lager and Gibbs (1973) caution should be exercised in making inferences about the nature of the bonding just because one or more of these parameters provide a plausible interpretation of bond length variations. Similar caveats have been made by others including Bent (1968), Gibbs et al. (1972) and Brown and Shannon (1973).

Acknowledgements. We are pleased to thank the National Science Foundation for supporting this work with grant EAR82-18743, Virginia Chapman for preparing the manuscript and Sharon Chiang for drafting the figures. VPI&SU is also thanked for defraying the computing costs incurred in this study. Z.G. Zhang wishes to express his appreciation to the Department of Geological Sciences at VPI&SU and to Dr. G.V. Gibbs for the hospitality he received during his visit. He also wishes to thank the People's Republic of China for awarding him a Fellowship to study Quantum Mineralogy at VPI&SU where this study was completed. Mickey Gunter is thanked for providing the ORTEP drawing of andalusite displayed in Figure 4.

References

Baur W (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. Trans Am Crystallogr Assoc 6:125–155

Bent HA (1968) Tangent-sphere models of molecules: VI. Ion-packing models of covalent compounds. J Chem Educ 45:768–778

Bondy JA, Murty USR (1976) Graph Theory with Applications. North-Holland, New York, p 264

Brown ID, Shannon RD (1973) Empirical bond-strength-bond-length curves for oxides. Acta Crystallogr A29:266–282

Cruickshank DWJ (1962) X-ray results on aromatic hydrocarbons. Tetrahedron 17:155–161

Geisinger KL, Gibbs GV, Navrotsky A (1985) A molecular orbital study of bond length and angle variations in framework structures. Phys Chem Minerals 11:266–283

Gibbs GV, D'Arco P, Boisen Jr. MB (1987a) Molecular mimicry of bond length and angle variations in germanate and thiogermanate crystals: A comparison with variations calculated for C-, Si-, Sn-containing oxide and sulfide molecules. J Phys Chem 91:5347–5354

Gibbs GV, Finger LW, Boisen Jr. MB (1987b) Molecular mimicry of the bond length-bond strength variations in oxide crystals. Phys Chem Minerals 14:327–331

Gibbs GV, Hamil MM, Louisnathan SJ, Bartell LS, Yow H (1972) Correlations between SiO bond length, SiOSi angle and bond overlap populations calculated using extended Huckel molecular orbital theory. Am Mineral 57:1578–1612

Gibbs GV, Meagher EP, Newton MD, Swanson DA (1981) A comparison of experimental and theoretical bond length and angle variations in minerals, inorganic solids and molecules. In: O'Keeffe M and Navrotsky A (eds) Structure and bonding in crystals, Vol. 1, Academic Press, New York, 195–225

Hehre WJ, Random L, Schleyer PR, Pople JA (1986) Ab initio molecular orbital theory. John Wiley and Sons Inc., New York, p 548

Lager GA, Gibbs GV (1973) Effect of variations in OPO and POP angles on PO bond overlap populations for some selected ortho- and pyrophosphates. Am Mineral 58:756–764

Pauling L (1929) The principles determining the structure of complex ionic crystals. J Am Chem Soc 51:1010–1026

Pauling L (1952) Interatomic distances and bond character in the oxygen acids and related substances. J Phys Chem 56:361–365

Pauling L (1960) The nature of the chemical bond. 3rd edition, Cornell University Press, Ithaca, New York, p 644

Pauling L, Brockway LO (1937) Carbon-carbon bond distances. The electron diffraction investigation of ethane, propane, isobutane, neopentane, cyclopropane, cyclopentane, cyclohexane, allene, ethylene, isobutene, tetramethylethylene, mesitylene, and hexamethylbenzene. J Am Chem Soc 59:1223–1236

Pauling L, Brockway LO, Beach JY (1935) The dependence of interatomic distance on single bond-double bond resonance. J Am Chem Soc 57:2705–2709

Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr A32:751–767

Shannon RD, Prewitt CT (1969) Effective ionic radii in oxides and fluorides. Acta Crystallogr B25:925–946

Zoltai T, Stout JH (1984) Mineralogy concepts and principles. Burgess Publishing Co., Minneapolis, Minnesota, p 505

Received June 26, 1987