

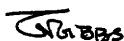
BOND LENGTH AND BONDED RADII VARIATIONS IN NITRIDE MOLECULES  
AND CRYSTALS

by

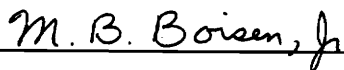
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Thesis submitted to the Faculty of the  
Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE  
in  
Geological Sciences

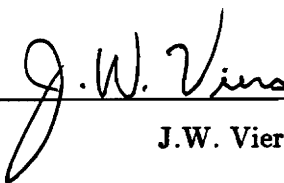
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August, 1990  
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# BOND LENGTH AND BONDED RADII VARIATIONS IN NITRIDE MOLECULES AND CRYSTALS

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Lewis A. Buterakos

G.V. Gibbs, Chairman  
Geological Sciences

(ABSTRACT)

Molecular Orbital calculations on 31  $H_{3x-m}X^{m+}N_x$  hydronitride molecules containing 3-, 4-, and 6-coordinate  $X$ -cations from rows 1-4 of the periodic table yield minimum energy bond lengths,  $R_t(XN)$ , which reproduce observed bond lengths,  $R_o(XN)$ , in crystalline nitrides to within  $0.03\text{\AA}$ , on average. A linear regression analysis of  $\ln[R_t(XN)]$  vs.  $\ln(p)$  with  $p = s/r$ , where  $s$  is the Pauling bond strength and  $r$  is the row number of the  $X$ -cation in the periodic table, gives the equation  $R(XN) = 1.47p^{-0.24}$ , which is shown to reproduce the observed  $XN$  bond lengths of Baur (1987) to within  $0.09\text{\AA}$ , on average. This equation is statistically identical to the equation  $R(XN) = 1.49p^{-0.22}$ , derived from a linear regression analysis of  $\ln[R_o(XN)]$  vs.  $\ln(p)$ , and is similar in form to those obtained for the oxides ( $R(XO) = 1.39p^{-0.22}$ ) and the sulfides ( $R(XS) = 1.83p^{-0.21}$ ).

Bonded radii obtained from theoretical electron density maps of 13 tetrahedral  $H_{12-m}X^{m+}N_4$  hydronitride molecules for both  $X$ -cation and nitrogen anion show a linear relationship with bond length similar to that observed for the oxides and the sulfides. The bonded radius of N varies from 0.89Å in  $H_8CN_4$  to 1.37Å in  $H_{11}NaN_4$ , but is smaller in all cases considered than the effective ionic radii for N (1.42Å- 1.54Å) given by Baur (1987). The departure of the C radius from the bonded radius – bond length trends for the 3- and 4-coordinate first row  $X$ -cations is thought to be related to the covalence of the CN bond, since similar occurrences are observed for the PS and NO bonds in the sulfides and oxides.

Bonded radii of Si and O obtained from theoretical electron density maps,  $r(Si)_t$  and  $r(O)_t$ , of  $H_6Si_2O_7$  and  $H_8SiO_6$  differ from those obtained from experimental electron density maps,  $r(Si)_o$  and  $r(O)_o$ , of coesite and stishovite by 0.02Å, on average. Plots of  $r(O)$  and  $r(Si)$  vs.  $R(SiO)$  for both theoretical and experimental data shows that changes in the bonded radius of oxygen from 4-coordinate Si to 6-coordinate Si are over three times as great as those observed for silicon. This result suggests that variation in the size of the anion may play a more significant role in bond length variation with cation coordination than previously suspected.

## ACKNOWLEDGEMENTS

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## INTRODUCTION

The success of molecular orbital (MO) calculations on model molecular systems in reproducing bond length and angle variations, gross features of electron density distributions, spectra, thermodynamic and physical properties observed in crystalline and non-crystalline solids has been well documented. Newton and Gibbs (1980), using a minimal STO-3G basis on disilicic acid molecule, were able to reproduce bond length and angle trends observed in silicates and siloxanes. In a related work, O'Keeffe *et al.*, (1980) successfully modeled the SiSi nonbonded interactions, SiO stretch and the bulk modulus of low quartz using interatomic force constants derived from STO-3G calculations on the molecule. In a subsequent review article, Gibbs (1982) showed that extended basis 6-31G\* calculations on model molecules generated bonding peaks in electron density which are qualitatively similar in magnitude and position to those observed in silicates. In an application to glasses and melts, Navrotsky *et al.*, (1985), suggested that the ease of glass formation can be ascribed to the compliance of the  $TOT$  angle ( $T = \text{Si,Al}$ ) as determined by MO calculations on appropriate molecular fragments. Application of MO methods to thiosilicates (Geisinger and Gibbs 1981), nitrides (Julian and Gibbs 1985), borates (Zhang *et al.*, 1985), phosphates (O'Keeffe *et al.*, 1985), silicates and aluminosilicates (Geisinger *et al.*, 1985), germanates, thiogermanates, stannates, and thio-stannates (Gibbs *et al.*, 1987a), sulfates (Lindsay and Gibbs 1988), and sulfides (Bartelmehs *et al.*, 1989) has met with similar success in qualitatively modeling bond length and angle variations in those mineral groups. The similarity in bonding features between energy optimized molecules and chemically similar crystals coupled with the ability of molecule based models to reasonably predict physical properties of crystalline and non-crystalline solids suggests that bonding in solids is controlled by short-range forces similar to those

found in molecules.

In a specific application of this postulate, Gibbs (1982) was able to show that MO calculations on first and second row hydroxyacid molecules yielded bond length – bond strength curves that qualitatively reproduce those derived experimentally by Brown and Shannon (1973) for oxides. In subsequent work, Gibbs *et al.*, (1987b) defined a new bond parameter  $p = s/r$ , where  $s$  is the bond strength as defined by Pauling (1929) and  $r = 1, 2, 3, \dots$  for first-, second-, third-, ... row main group  $X$ -cations, respectively. They found that 99% of the variation in  $\ln[R(XO)]$  for first and second row  $XO$  bonds can be explained in terms of a linear dependence on  $\ln(p)$ . Boisen *et al.*, (1988) were also able to show a similar correlation for bond numbers calculated from large (up to 50 atoms) molecular fragments from ten different silicate crystals, supporting the assertion that bond number and Pauling bond strength measure similar properties of a bond. Concurrent with this work, Finger and Gibbs (1985) derived a set of bonded radii for first and second row  $X$ -cations from electron density maps of hydroxyacid molecules optimized in a 6-31G\* basis. Radii obtained in this manner vary linearly with bond length and the crystal radii of Shannon (1976) and compare rather well with bonded radii obtained from experimental electron density maps of crystals.

To determine whether similar trends might exist for other anions, Bartelmehs (1987) and Bartelmehs *et al.*, (1989) undertook a study of bond length and bonded radii variations in sulfide molecules and crystals. As with the oxides, strong correlations were found between  $\ln[R(XS)]$  and  $\ln(p)$ ,  $r(X)$  and  $R(XS)$ ,  $r(S)$  and  $R(XS)$ , and between  $r(X)$  and the sulfide radii of Shannon (1981). Also, in a preliminary examination of nitride crystals (Bartelmehs 1987), a similar correlation was found to obtain for 33  $XN$  bond lengths and the bond parameter  $p$ . This observation, together with the success of molecular orbital methods in mimicing



bond length and angle variations and local geometries in silicon nitrides (Julian and Gibbs 1985) and methyl- and silyl- substituted amines (Julian and Gibbs 1988), suggests that similar bond length and bonded radii trends may exist for nitrides as well. The present work was undertaken to learn whether the bond length – bond strength and bonded radii systematics observed in oxides and sulfides are also present in nitrides.

## MOLECULAR ORBITAL CALCULATIONS ON HYDRONITRIDE MOLECULES

Molecular orbital calculations were completed on 31  $\text{H}_{3\nu-m}\text{X}^{m+}\text{N}_\nu$  hydronitride molecules containing 3-, 4-, and 6-coordinate main group X-cations from rows one through four of the periodic table. A 6-31G\* basis and 31G basis were used on N and H, respectively, in all calculations. A 6-31G\* basis was used on the first row cations  $\text{Li}^+$  through  $\text{C}^{4+}$  and second row cations  $\text{Na}^+$  through  $\text{S}^{6+}$ . The 3-21G\* basis of Dobbs and Hehre (1986) was used on all third and fourth row main group cations for which calculations were done. Molecular geometries of the  $\text{XN}_\nu$  coordinated polyhedra were clamped at the ideal values for triangular, tetrahedral, and octahedral coordination with dihedral angles of  $\text{NH}_x$  groups ( $x = 1,2,3$ ) chosen such as to minimize H...H interactions. All XN bonds within a given molecule were constrained to be equal, as were all NH bonds and XNH angles associated with a particular type of  $\text{NH}_x$  group. All XN and NH bonds and XNH angles were then optimized with the restricted Hartree-Fock procedure employed in the Gaussian 86 program (Frisch *et al.*, 1984). Optimization with the above basis sets yielded net positive charges on all cations and net negative charges on N. The bond lengths,  $R_t(\text{XN})$ , calculated for the XN bonds in the molecules are listed in Table I and compared with observed values obtained from tables of effective ionic radii (Baur 1987).

Figure 1 shows a plot of observed XN bond lengths,  $R_o(\text{XN})$ , obtained using the effective ionic radii of Baur (1987) vs. the theoretical bond lengths,  $R_t(\text{XN})$ , calculated in this study. The  $R_t(\text{XN})$  values agree with the  $R_o(\text{XN})$  values to within 0.03Å, on average. A regression analysis shows that about 99% of the variation in  $R_o(\text{XN})$  can be explained in terms of a linear dependence on  $R_t(\text{XN})$ , with a slope and intercept statistically identical to 1 and 0, respectively. The

close agreement between the  $R_t(XN)$  and  $R_o(XN)$  values, as with oxides and sulfides, is believed to reflect the similar nature of bonding forces in molecules and crystals.

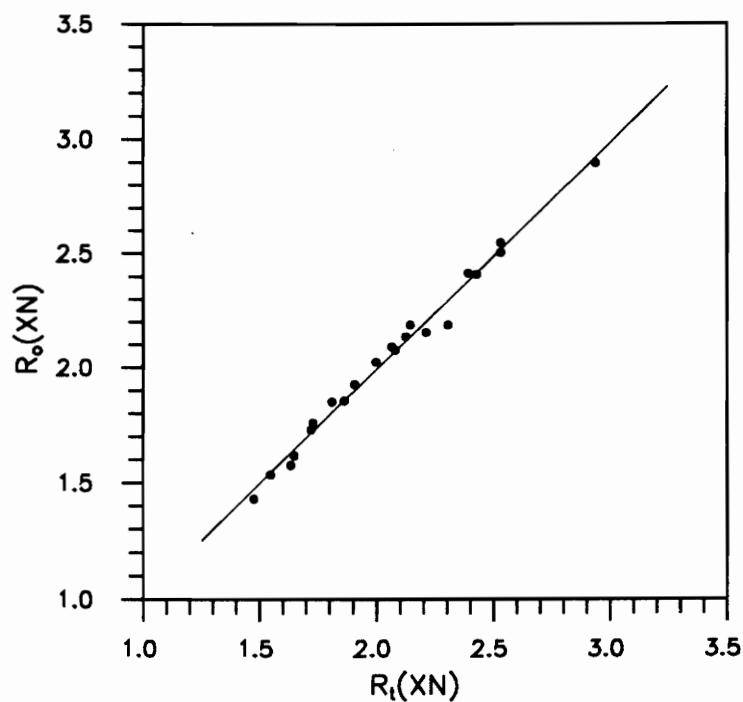


Figure 1. Observed  $XN$  bond lengths,  $R_o(XN)$ , obtained using the effective ionic radii of Baur (1987) vs. the theoretical bond lengths,  $R_t(XN)$ , obtained in this study. The regression equation is  $R_o(XN) = 0.01 + 0.99 R_t(XN)$ , with coefficient of determination  $r^2 = 0.99$ .

Table I. Theoretical,  $R_t(XN)$ , and observed,  $R_o(XN)$ ,  $XN$  bond lengths, effective ionic radii,  $r(X)_c$ , of Baur (1987), cation,  $r(X)$ , and nitrogen,  $r(N)$ , bonded radii for  $XN_v$  coordinated polyhedra of molecules examined in this study.

Molecule	$X^vN$	$R_t(XN)$	$R_o(XN)$	$r(X)_c$	$r(X)$	$r(N)$
$H_8LiN_3$	$Li^{III}N$	2.00	2.02	0.57	0.70	1.30
$H_7BeN_3$	$Be^{III}N$	1.65	1.62	0.17	0.57	1.08
$H_6BN_3$	$B^{III}N$	1.48	1.43	-0.01	0.51	0.97
$H_5CN_3$	$C^{III}N$	1.34			0.50	0.84
$H_{11}LiN_4$	$Li^{IV}N$	2.08	2.08	0.62	0.75	1.33
$H_{10}BeN_4$	$Be^{IV}N$	1.73	1.76	0.31	0.60	1.13
$H_9BN_4$	$B^{IV}N$	1.55	1.54	0.09	0.52	1.02
$H_8CN_4$	$C^{IV}N$	1.44			0.55	0.89
$H_{11}NaN_4$	$Na^{IV}N$	2.39	2.42	0.96	1.02	1.37
$H_{10}MgN_4$	$Mg^{IV}N$	2.06	2.09	0.64	0.87	1.19
$H_9AlN_4$	$Al^{IV}N$	1.86	1.86	0.41	0.79	1.07
$H_8SiN_4$	$Si^{IV}N$	1.72	1.73	0.29	0.72	1.00
$H_7PN_4$	$P^{IV}N$	1.63	1.58	0.14	0.68	0.96
$H_6SN_4$	$S^{IV}N$	1.59			0.66	0.93
$H_{10}CaN_4$	$Ca^{IV}N$	2.43	2.41	0.96	1.20	1.23
$H_9GaN_4$	$Ga^{IV}N$	1.91	1.93	0.48	0.95	0.96
$H_8GeN_4$	$Ge^{IV}N$	1.81	1.85	0.41	0.88	0.93
$H_9InN_4$	$In^{IV}N$	2.12	2.14			
$H_{17}LiN_6$	$Li^{VI}N$	2.30	2.19			
$H_{16}BeN_6$	$Be^{VI}N$	1.98				
$H_{15}BN_6$	$B^{VI}N$	1.80				
$H_{14}CN_6$	$C^{VI}N$	1.70				
$H_{17}NaN_6$	$Na^{VI}N$	2.53	2.55			
$H_{16}MgN_6$	$Mg^{VI}N$	2.21	2.15			
$H_{15}AlN_6$	$Al^{VI}N$	2.02				
$H_{14}SiN_6$	$Si^{VI}N$	1.88				
$H_{13}PN_6$	$P^{VI}N$	1.79				
$H_{12}SN_6$	$S^{VI}N$	1.73				
$H_{17}KN_6$	$K^{VI}N$	2.94	2.90			
$H_{16}CaN_6$	$Ca^{VI}N$	2.53	2.50			
$H_{14}SnN_6$	$Sn^{VI}N$	2.14	2.19			

## BOND LENGTH – BOND PARAMETER CORRELATIONS

When observed mean interatomic distances in nitrides,  $R_o(XN)$ , containing main group  $X$ -cations from rows 1-5 of the periodic table are estimated by sums of effective ionic radii of Baur (1987), it is found that  $p$  ranks  $R_o(XN)$  with success comparable to that observed for the oxides (Gibbs and Boisen 1986, Gibbs *et al.*, 1987b) and sulfides (Bartelmehs 1987, Bartelmehs *et al.*, 1989) (Figure 2a). A regression analysis of  $\ln[R_o(XN)]$  vs.  $\ln(p)$  (Figure 2b) reveals that 98% of the variation in  $\ln[R_o(XN)]$  can be explained in terms of a linear dependence on  $\ln(p)$ , giving the equation

$$R(XN) = 1.49p^{-0.22}. \quad (1)$$

The parameters of this equation (1.49 and  $-0.22$ ) compare rather well with those (1.43 and  $-0.22$ ) reported for  $XN$  bonds by Bartelmehs (1987). Figure 3a shows a similar plot for the theoretical bond lengths obtained in the MO calculations as a function of  $p$ . A linear regression analysis of  $\ln[R_t(XN)]$  vs.  $\ln(p)$  (Figure 3b) for these data gives a coefficient of determination  $r^2$  of 0.97 and the equation

$$R(XN) = 1.47p^{-0.24} \quad (2)$$

which is statistically identical to Equation (1). When Equation (2) is used to calculate  $R(XN)$  for observed values of  $p$ , it is found to reproduce  $R_o(XN)$  values to within  $0.09\text{\AA}$ , on average. Figure 4 shows a plot of the observed bond lengths,  $R_o(XN)$ , vs. the calculated bond lengths,  $R_c(XN)$ , obtained from Equation (2). A regression analysis shows that 97% of the variation in  $R_o(XN)$  can be explained in terms of a linear dependence on the calculated bond length  $R_c(XN)$ , with a slope and intercept of 0.89 (esd = 0.03) and 0.21 (esd = 0.07), respectively. This agreement in bond lengths is in accord with that obtained for oxides (Gibbs *et al.*, 1987b) and sulfides (Bartelmehs *et al.*, 1989).

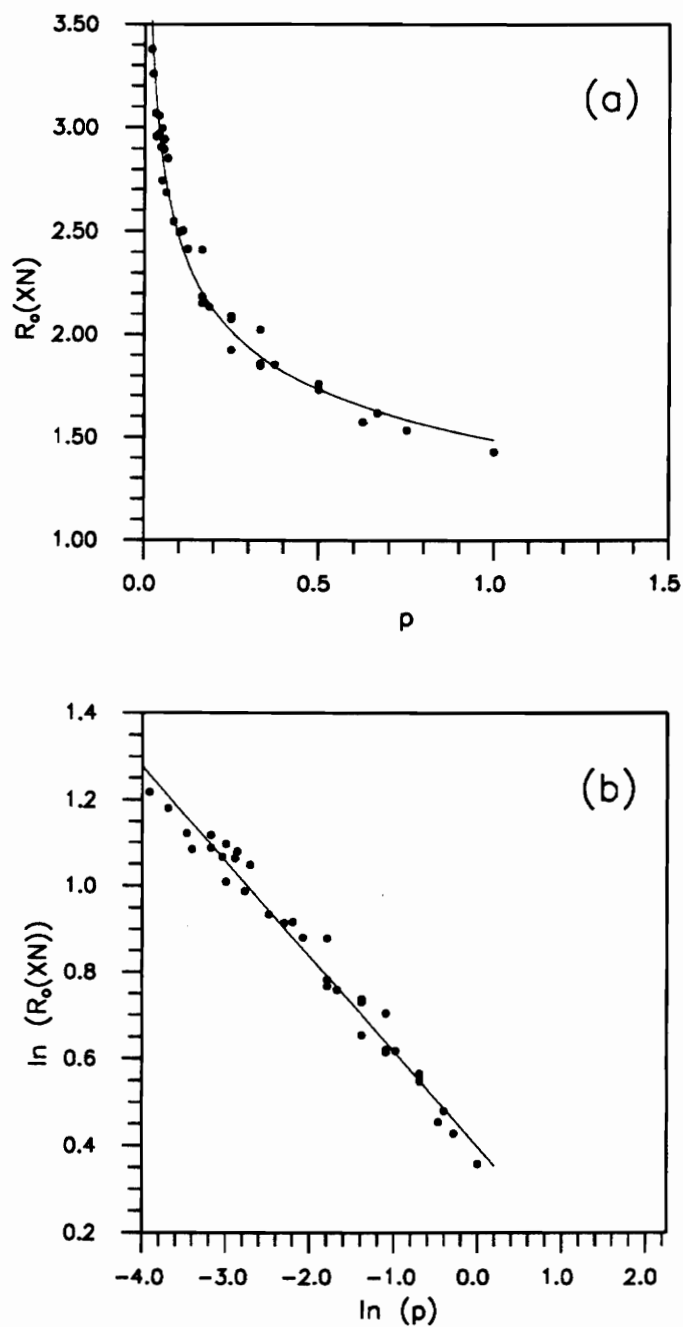


Figure 2. (a) Observed  $XN$  bond lengths,  $R_o(XN)$ , published by Baur (1987) vs. the bond parameter  $p = s/r$ , where  $s$  is the Pauling bond strength and  $r$  is the row number of the  $X$ -cation. (b)  $\ln[R_o(XN)]$  vs.  $\ln(p)$ . The regression equation is  $\ln[R_o(XN)] = 0.40 - 0.22 \ln(p)$ , with coefficient of determination  $r^2 = 0.98$ .

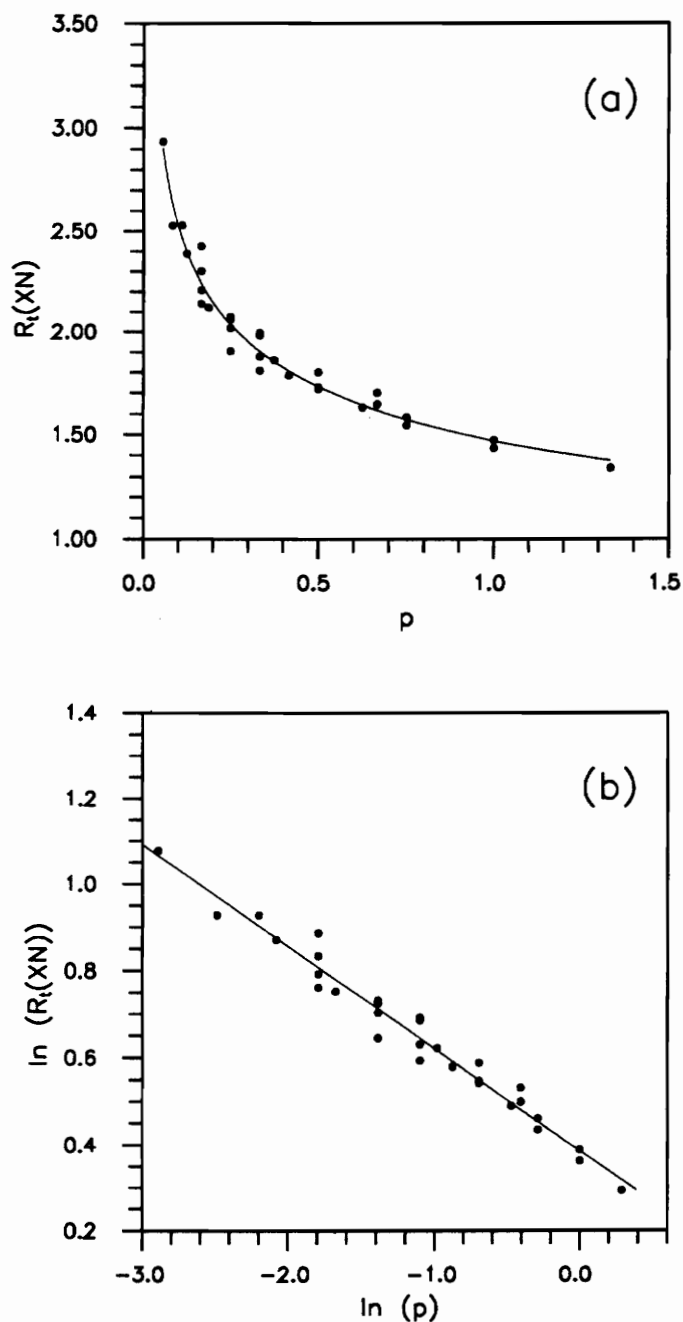


Figure 3. (a) Theoretical XN bond lengths,  $R_t(XN)$ , obtained from MO calculations on hydronitride molecules vs. the bond parameter  $p = s/r$ , where  $s$  is the Pauling bond strength and  $r$  is the row number of the X-cation. (b)  $\ln[R_t(XN)]$  vs.  $\ln(p)$ . The regression equation is  $\ln[R_t(XN)] = 0.39 - 0.24 \ln(p)$ , with coefficient of determination  $r^2 = 0.97$ .

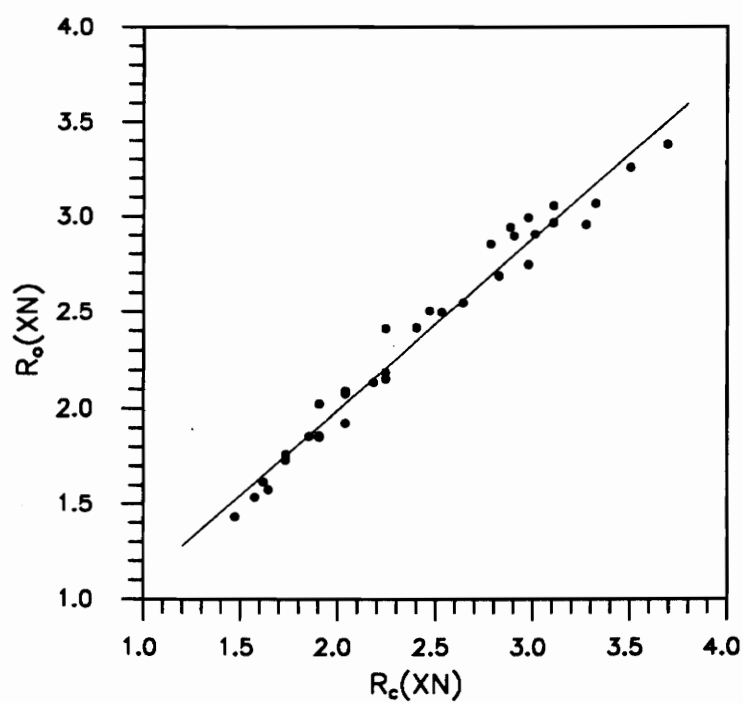


Figure 4. Observed  $XN$  bond lengths,  $R_o(XN)$ , published by Baur (1987) vs. calculated  $XN$  bond lengths,  $R_c(XN)$ , obtained with the equation  $R(XN) = 1.47p^{-0.24}$ . The regression equation is  $R_o(XN) = 0.21 + 0.89 R_c(XN)$ , with coefficient of determination  $r^2 = 0.97$ .



## ELECTRON DENSITY DISTRIBUTIONS AND BONDED RADII

The concept of ionic radius has been particularly useful in applications to crystal structure determination and crystal chemistry (Pauling 1927, 1929, 1960, Shannon and Prewitt 1969, 1970, Shannon 1976, 1981, Baur 1987). However, in spite of its success, some authors (Slater 1965, Shannon and Prewitt 1969, Prewitt 1982) have proposed that ionic radii may not be realistic indicators of the sizes of atoms in crystals. For instance, Gourary and Adrian (1960) found it necessary to define ionic radii for Na, Cl, Li, and F by the distance from the atomic center to the minimum in electron density as measured along the bond in order to obtain more realistic approximations of vacancy sizes in alkali halides. Radii obtained by this method are termed bonded radii by Bader *et al.*, (1971) and are generally more realistic in the context of a crystal since they are obtained directly from the charge distribution about the atoms.

This consideration led Finger and Gibbs (1985) to derive a set of bonded radii for first and second row main group  $X$ -cations from total electron density maps of energy optimized hydroxyacid molecules. Plots of these radii vs. the optimized  $XO$  bond lengths were found to be linear, with approximately parallel trends for the first and second row  $X$ -cations. Similar plots for the bonded radius of oxygen were also linear, with the oxygen radius, rather than being constant, varying according to the relation

$$r(O) = (0.35 - 0.1r) + \frac{1}{2}R_t(XO) \quad (3)$$

where  $r = 1, 2$  for first and second row  $X$ -cations, respectively (Gibbs and Boisen 1986). This result verifies the remarks of Shannon and Prewitt (1969), who suggest the bonded radius of oxygen may vary with the type of  $X$ -cation bonded to it. Bartelmehs (1987) and Bartelmehs *et al.*, (1989) conducted a similar study for

sulfides and observed bonded radii variations comparable to those observed in oxides. In particular, the variation in the bonded radius of the sulfur anion,  $r(\text{S})$ , was related to row number  $r$  and  $R_t(\text{XS})$  by

$$r(\text{S}) = (0.59 - 0.13r) + \frac{1}{2}R_t(\text{XS}). \quad (4)$$

The terms  $\frac{1}{2}R_t(\text{XS})$  and  $\frac{1}{2}R_t(\text{XO})$  were interpreted as indicating that bond length variations are shared equally between cation and anion, an idea further advanced by Lindsay and Gibbs (1988) in their study of bonded radii variations in sulfur-oxygen coordinated polyhedra. The variable radius of oxygen in oxides and sulfur in sulfides is contrary to the assumption of constant anion radius made in the derivation of ionic radii (Pauling 1927, 1929, 1960, Shannon and Prewitt 1969, Shannon 1976, 1981), but it is consistent with the work of Paschalis and Weiss (1969) and Johnson (1973, 1975).

For this study, total electron density maps for thirteen  $\text{H}_{12-m}\text{X}^m\text{N}_4$  tetrahedral molecules were calculated using the program DENMAP (written by R. Stevens and modified by J. A. Tossell and L. W. Finger) and density matrices obtained in Gaussian 86 Hartree-Fock single-point calculations at the optimized geometries. The minima in the electron density along the bonds were determined by finding the minima of a polynomial fit to the density contours using the programs QUARTIC and QSOLVE (written by M. B. Boisen, Jr.). Figure 5 shows the resultant bonded radii of the cations and nitrogen plotted against the optimized  $\text{XN}$  bond length. It is clear from these plots that the linearity observed in similar plots for oxides and sulfides also obtains for nitrides. The linear relationship between  $r(\text{N})$  and  $R_t(\text{XN})$  is consistent with the findings of O'Keeffe (1979), who showed the apparent radius of nitrogen varied linearly with interionic distance in nitrides with the rock salt structure type. A linear regression analysis

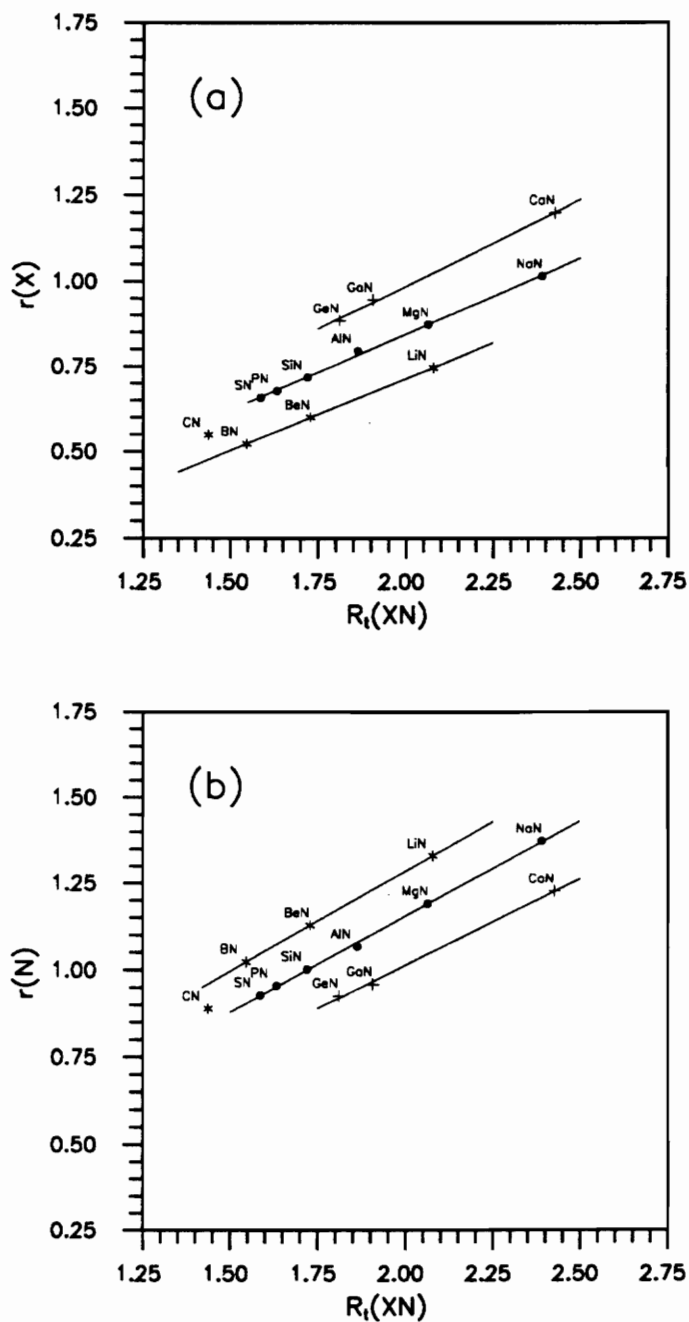


Figure 5. Plots of (a) cation bonded radii,  $r(X)$ , and (b) the bonded radius of nitrogen,  $r(N)$ , vs. the theoretical bond lengths,  $R_t(XN)$ , obtained from MO calculations on hydronitride molecules containing first (\*), second (•), and third (+) row main group cations.

of the bonded radius of nitrogen as a function of  $X$ -cation row number,  $r$ , and the optimized bond length,  $R_t(XN)$ , gives an  $r^2$  of 0.97 and the equation

$$r(N) = (0.26 - 0.13r) + 0.57R_t(XN) \quad (5)$$

which reproduces the observed values of  $r(N)$  to within  $0.02\text{\AA}$ , on average. As with oxides and sulfides, the coefficient of  $R_t(XN)$  indicates that variation in  $XN$  bond length is shared more or less equally by both cation and nitrogen. The nitrogen radius varies from  $0.89\text{\AA}$  in  $H_8CN_4$  to  $1.37\text{\AA}$  in  $H_{11}NaN_4$  (see Table I), a difference of  $0.48\text{\AA}$ . Since the average coordination of a nitrogen atom in a  $H_{12-m}X^m+N_4$  tetrahedral molecule is  $4 - \frac{m}{4}$ , the maximum variation expected in the ionic radius

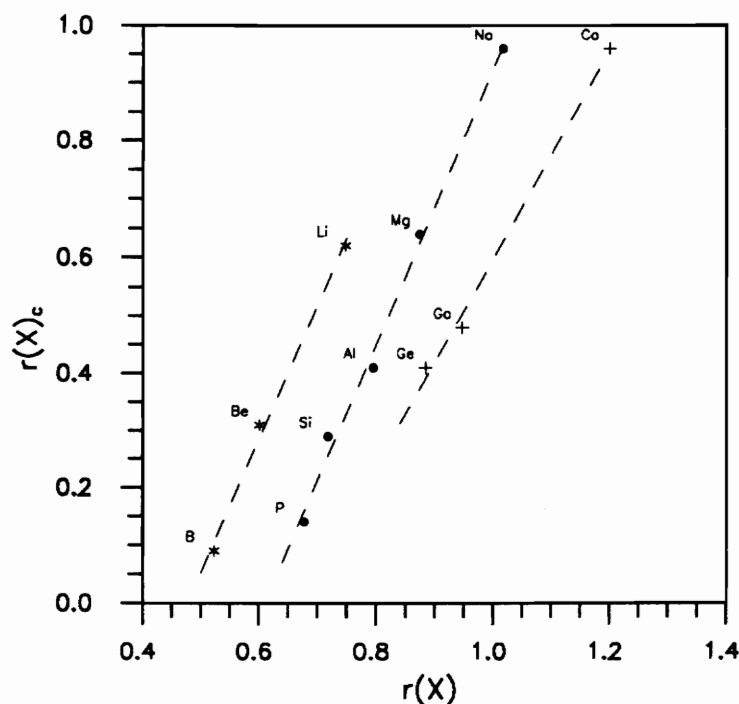


Figure 6. A plot of the effective ionic radii,  $r(X)_c$ , of Baur (1987) vs. the cation bonded radii,  $r(X)$ , for first (\*), second (•), and third (+) row main group cations.

of nitrogen (for  $m = 1, 2, 3, 4, 5, 6$ ) is less than  $0.04 \text{ \AA}$  (Baur 1987). Thus the variation in  $XN$  bond length with  $X$ -cation must be largely accounted for by variation in  $r(X)_c$ , with the result that  $r(X)_c$  will vary about twice as much as  $r(X)$  with different  $X$ -cations. Figure 6 bears this out. A linear regression analysis of  $r(X)_c$  as a function of cation row number  $r$  and bonded radius  $r(X)$  gives a coefficient of 2.16 for  $r(X)$ , indicating that changes in  $r(X)_c$  are about twice that observed for  $r(X)$ . It is apparent from the above considerations that while ionic radii may serve very well in reproducing bond lengths, they are probably not realistic indicators of atomic sizes in crystals (Bartelmehs *et al.*, 1989).

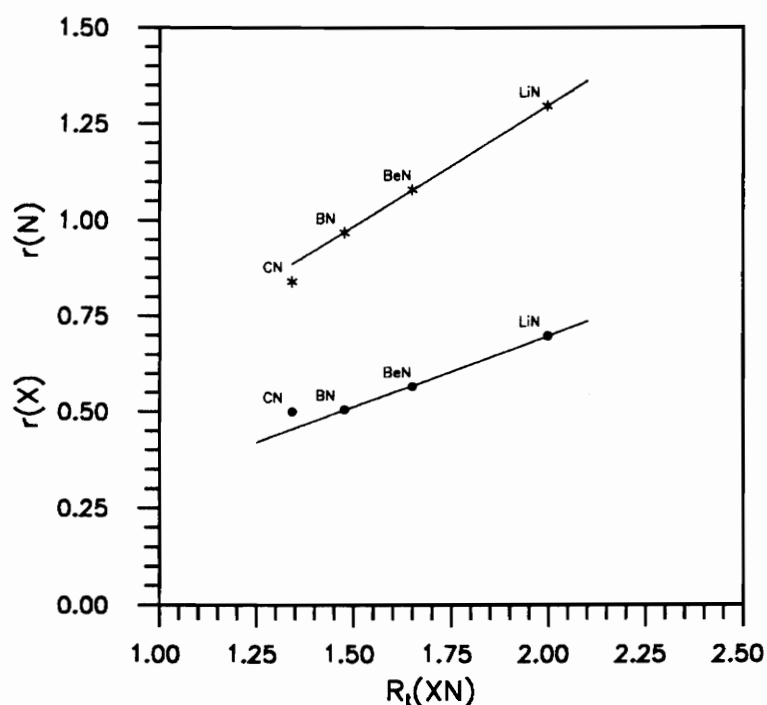


Figure 7. Plot of cation bonded radius (●),  $r(X)$ , and the bonded radius of nitrogen (\*),  $r(N)$ , vs. the theoretical bond lengths,  $R_t(XN)$ , for 3-coordinate first row nitrides.

The departure of the bonded radius of C from the regression line in Figure 5 is noted with some interest. Since a similar departure observed for the bonded radius of P in sulfides was attributed to the decreased ionicity of the PS bond (Bartelmehs 1987), similar departures should be present for the bonded radius of C in 3-coordinate first row nitrides and for the bonded radius of N in 4-coordinate first row oxides. To ascertain whether such departures obtain in these systems as well, bonded radii were determined for the cations and anion in four first row  $H_{9-m}X^{m+}N_3$  molecules and tetrahedral  $H_3NO_4$ . The bonded radii of the cations and oxygen for the remaining oxides were obtained from Finger and Gibbs

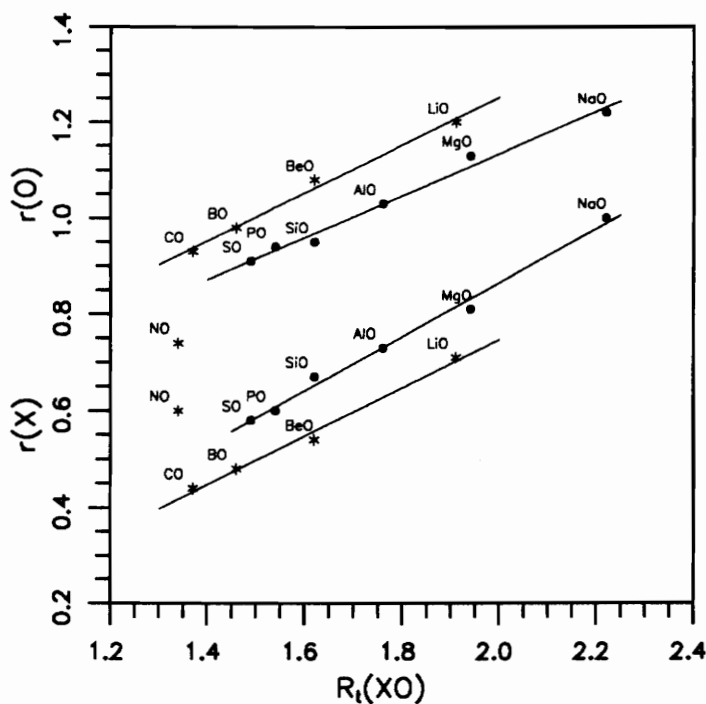


Figure 8. Plots of cation bonded radii,  $r(X)$ , and the bonded radius of oxygen,  $r(O)$ , vs. the theoretical bond lengths,  $R_t(XO)$ , for first (\*) and second (•) row main group cations (Finger and Gibbs 1985, Gibbs and Boisen 1986, Gibbs *et al.*, 1987b).

(1985). Figure 7 shows that  $r(\text{C})$  departs from the trend of the remaining data in 3-coordinate first row nitrides and  $r(\text{N})$ , where N is a cation, departs in 4-coordinate first row oxides (Figure 8). In each case, the departures occur for bonded radii obtained from charge distributions of bonds formed between adjacent atoms in the periodic table, and correspond to a relative shift in the minimum in electron density toward the more electronegative atom. This is understandable, since the minimum in electron density along a bond is sensitive to the degree of electron delocalization and charge transfer in the bond (Bader *et al.*, 1971), which presumably are larger and smaller, respectively, for bonded atoms in the same row belonging to adjacent groups. A second regression analysis of the nitrogen bonded radius in tetrahedral molecules without the carbon data point gave the equation

$$r(\text{N}) = (0.33 - 0.13r) + 0.54R_t(\text{XN}) \quad (6)$$

with  $r^2 = 0.99$ . This equation reproduces  $r(\text{N})$  to within  $0.01\text{\AA}$ , on average, and in view of the above consideration, is probably more representative of the overall trend of the data.

## COMPARISON OF EXPERIMENTAL AND THEORETICAL BONDED RADII

Gibbs and Boisen (1986) were able to show reasonable agreement between bonded radii calculated from total electron density maps of  $\text{H}_4\text{SiO}_4$  and  $\text{H}_8\text{SiO}_6$  molecules and similar radii obtained from electron density maps calculated from structure refinements of stishovite and coesite. While it would be desirable to make similar comparisons between bonded radii obtained in this study and radii obtained directly from total electron density maps of crystalline nitrides, the paucity of such maps makes this infeasible at present. However, since precise electron density maps exist for coesite (Geisinger *et al.*, 1987) and stishovite (Spackman *et al.*, 1987), a more detailed comparison of bonded radii from theoretical maps and bonded radii from the experimental maps contained in these papers was attempted.

Theoretical radii for silicon and oxygen were obtained using the  $\text{H}_6\text{Si}_2\text{O}_7$  molecule optimized by Gibbs *et al.*, (1988) and the optimized geometry for  $\text{H}_8\text{SiO}_6$ . The  $\text{SiO}_6$  distances and  $\text{SiOSi}$  angle of  $\text{H}_6\text{Si}_2\text{O}_7$  were fixed at the values observed for the five nonequivalent  $\text{SiOSi}$  groups in coesite (Geisinger *et al.*, 1987). The ideal octahedral geometry of  $\text{H}_8\text{SiO}_6$  was retained but  $\text{SiO}$  distances were fixed to the values and arrangement found in the Si octahedron of stishovite (Spackman *et al.*, 1987). A Gaussian 86 Hartree-Fock single-point calculation was done for  $\text{H}_8\text{SiO}_6$  and each  $\text{H}_6\text{Si}_2\text{O}_7$  configuration and resulting density matrices used to calculate total electron density maps for each molecule. Bonded radii for Si and O were then determined as described for the nitrides. However, since the experimental maps of coesite and stishovite were plotted with exponential contours, the minima in electron density between bonded atoms of these maps were obtained by measuring directly from the map.



Table II lists the bonded radii of silicon and oxygen obtained from the experimental and theoretical electron density maps. As can be seen, the bonded radius of O from the experimental maps,  $r(O)_o$ , is systematically larger than that obtained from the theoretical maps,  $r(O)_t$ , by  $0.02\text{\AA}$ , on average. Similarly,  $r(Si)_o$  is systematically smaller than  $r(Si)_t$  by  $0.02\text{\AA}$ , on average. Nevertheless, as Figure 9 shows, the radii compare well with each other, with regression slopes and intercepts statistically identical to 1 and 0 respectively.

Table II. Bonded radii of silicon and oxygen obtained from theoretical and experimental electron density maps of structural units from coesite and stishovite.

Bond	$R(\text{SiO})$	$r(\text{Si})_o$	$r(\text{O})_o$	$r(\text{Si})_t$	$r(\text{O})_t$
Si1O1	1.595	0.676	0.919	0.689	0.906
Si2O2	1.612	0.675	0.937	0.692	0.920
Si1O3	1.613	0.670	0.943	0.692	0.921
Si1O4	1.611	0.672	0.939	0.692	0.919
Si1O5	1.621	0.653	0.968	0.692	0.929
Si2O3	1.614	0.665	0.949	0.687	0.927
Si2O4	1.605	0.675	0.930	0.682	0.923
Si2O5	1.618	0.670	0.948	0.688	0.930
SiO (eq)	1.757	0.702	1.056	0.732	1.025
SiO (ax)	1.809	0.712	1.097	0.728	1.081

When  $r(O)_t$  and  $r(Si)_t$  are plotted against  $R(\text{SiO})$  (Figure 10), trends emerge which are similar to those obtained by Lindsay and Gibbs (1988) for sulfur-oxygen coordinated polyhedra. Regression analyses of the two data sets reveals that changes in the bonded radius of oxygen are over three times as great as changes in the bonded radius of silicon, a result contrary to the assumption made by Shannon and Prewitt (1969), Shannon (1976,1981), and Baur (1987), that the anion radius does not change with cation coordination number. While a similar

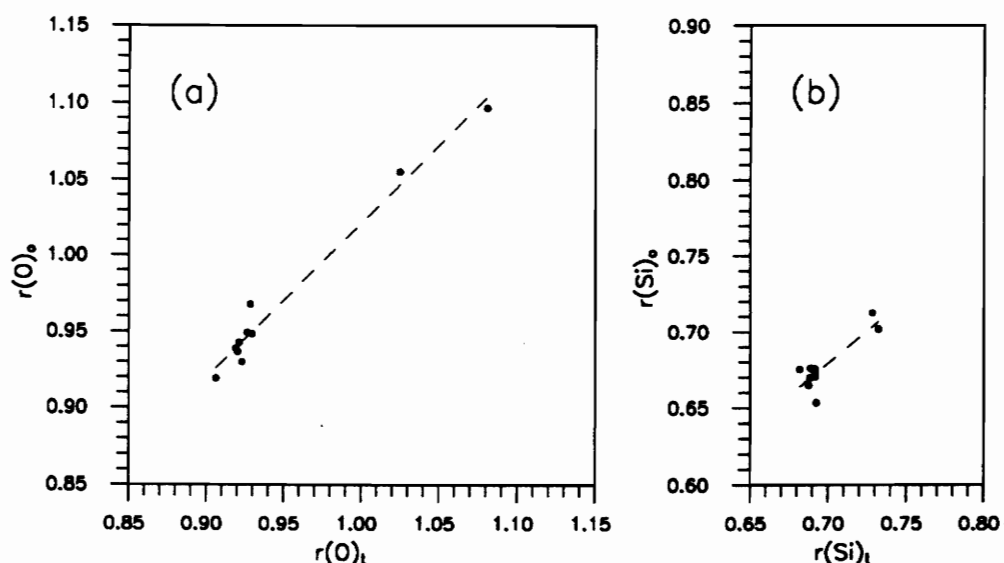


Figure 9. Plots of the bonded radius of oxygen and silicon from experimental electron density maps vs. bonded radius from theoretical electron density maps. (a)  $r(O)_o$  vs.  $r(O)_t$ . Slope and intercept are 1.019 (esd = 0.056) and 0.002 (esd = 0.053) respectively. (b)  $r(Si)_o$  vs.  $r(Si)_t$ . Slope and intercept are 0.851 (esd = 0.176) and 0.084 (esd = 0.123) respectively.

regression analysis led Lindsay and Gibbs (1988) to conclude that changes in the bonded radii of sulfur and oxygen with coordination number are about equal, close inspection of Figure 13 of that paper clearly shows trends which mimic roughly those in Figure 10 of this work. It is suspected that the outlying data point of the sulfur-oxygen bonded radii – bond length plot has a large influence on the regression analysis and thus the conclusion reached in Lindsay and Gibbs (1988).

Figure 11 shows a similar plot for the bonded radius of silicon and oxygen obtained from the experimental electron density maps of coesite and stishovite. The trends observed in Figure 10 for the bonded radii of silicon and oxygen are present in Figure 11 also. Regression analyses of the bonded radius of oxygen vs.

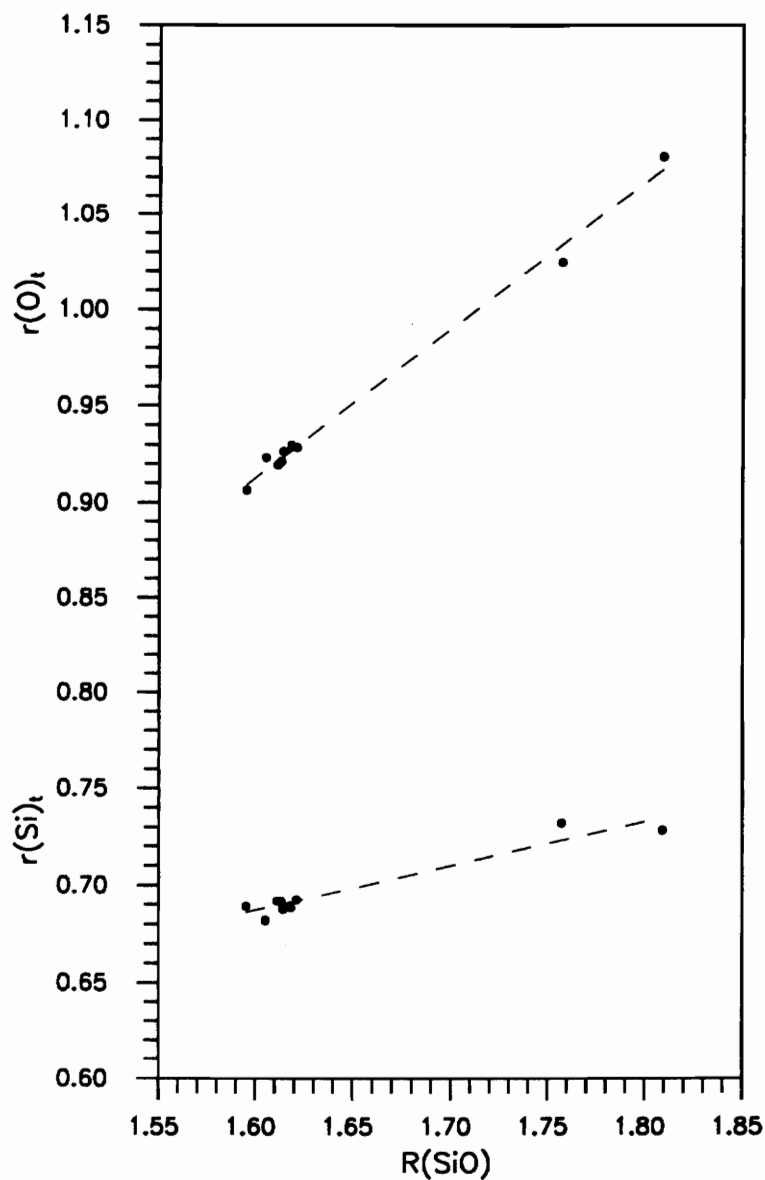


Figure 10. Plots of the bonded radius of oxygen and silicon from theoretical electron density maps vs. SiO bond length. Slope and intercept are 0.77 and -0.32, respectively, for  $r(\text{O})_t$  vs.  $R(\text{SiO})$ , and 0.23 and 0.32, respectively, for  $r(\text{Si})_t$  vs.  $R(\text{SiO})$ .

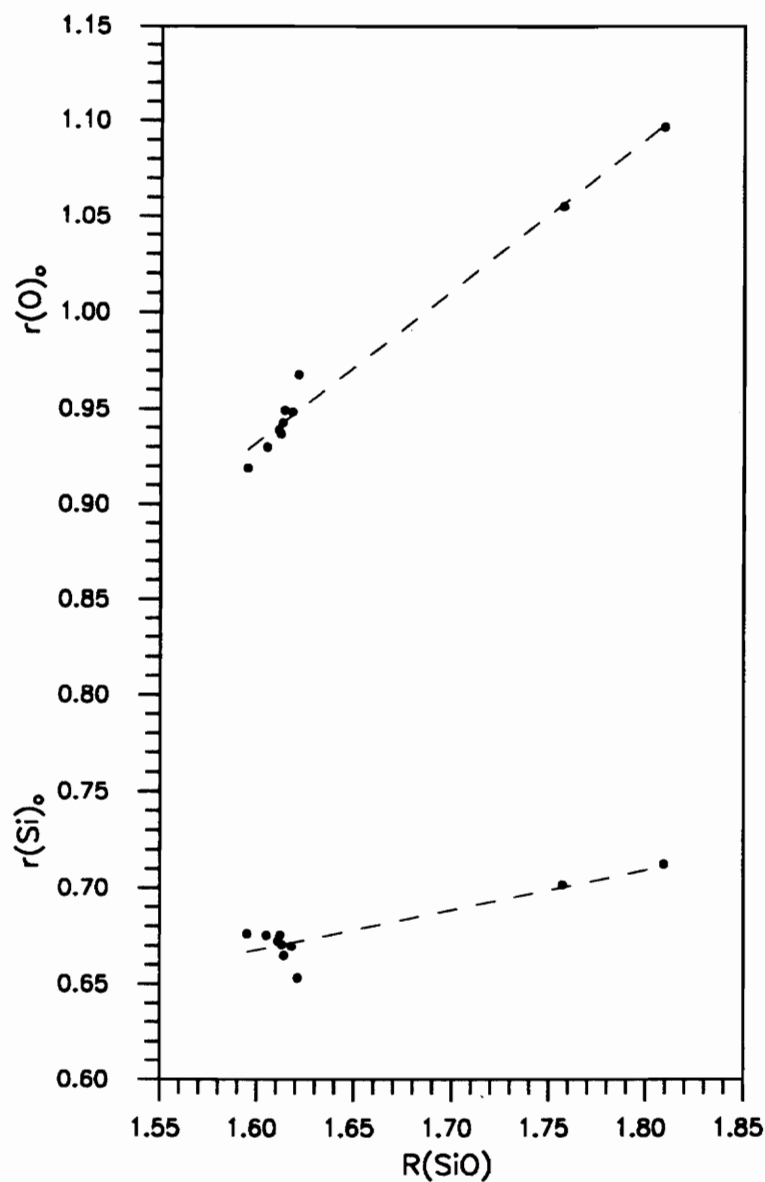


Figure 11. Plots of the bonded radius of oxygen and silicon from experimental electron density maps vs. SiO bond length. Slope and intercept are 0.79 and -0.33, respectively, for  $r(\text{O})_0$  vs.  $R(\text{SiO})$ , and 0.21 and 0.33, respectively, for  $r(\text{Si})_0$  vs.  $R(\text{SiO})$ .

the SiO bond length for the theoretical and observed radii reveal that the slopes and intercepts of the  $r(O)_t$  vs.  $R(\text{SiO})$  and  $r(O)_o$  vs.  $R(\text{SiO})$  plots are statistically identical. Similar analyses for the  $r(\text{Si})_t$  vs.  $R(\text{SiO})$  and  $r(\text{Si})_o$  vs.  $R(\text{SiO})$  plots show that the slopes and intercepts of these trends are also statistically identical. The similarity of the bonded radii variations in both experimental and theoretical electron density maps suggests that bonded radii obtained from theoretical maps may be adequate for crystal chemical work where approximate atomic sizes are needed.

## CONCLUSIONS

In this study, it was found that MO calculations on model molecules can reproduce observed  $XN$  bond lengths in nitride molecules and crystals. Both observed and theoretical  $XN$  bond lengths can be ranked by the bond parameter  $p$  with the same success obtained for oxides and sulfides. A prediction equation obtained from a regression analysis of the theoretical  $XN$  bond lengths reproduced observed  $XN$  bond lengths within  $0.09\text{\AA}$ , on average. The success of these methods substantiates the idea that bonding in solids behaves as if it is largely a short range phenomenon.

Bonded radii for the nitrogen anion and first, second, and third row main group cations calculated from theoretical electron density maps show the same linear relationship with bond length observed for oxides and sulfides. Variation in the  $XN$  bond was ascribed equally to variation in the size of the cation and nitrogen, contrary to the idea of constant anion radius assumed by many authors. The variation in the carbon radius from linearity in 3- and 4-coordinate nitrides is ascribed to increased covalence of the  $CN$  bond since similar effects were also observed for the  $PS$  and  $NO$  bonds.

A comparison of bonded radii calculated from theoretical and experimental electron density maps shows reasonably good agreement. The bonded radius of oxygen exhibited changes with silicon coordination over three times as great as those observed for the bonded radius of silicon. Because a similar interpretation can be made for sulfur-oxygen coordinated polyhedra, it is possible that variation in the size of the anion may play a more significant role in the variation of bond length with cation coordination than previously suspected.

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## VITA

I was christened Lewis Allen Buterakos on April 27, 1959, in the city of Winchester, Virginia, in honor of my uncle who died in the Korean War. After a childhood filled with butterfly-collecting, fossil-hunting, and star-gazing, I somewhat naively joined the U.S. Navy, where I served aboard the guided missile frigate U.S.S. Alywin. During May 1981, I sustained a severe twisting injury to my right knee, and was medically discharged in August 1982. Being eligible for higher education under the GI Bill, I enrolled in the Geology program at Virginia Tech in the Fall 1983 and received my B.S. degree in Geology during Summer session 1987. I started graduate work Fall quarter 1987 at Virginia Tech where I taught the laboratory portion of courses on Mathematical Crystallography, Systematics and Crystal Chemistry of Rock-forming Minerals, Optical Crystallography, and Geophysical Properties of Rocks and Minerals. During Fall semester 1989 I was supported by NSF grant EAR-8803933 to study bond length and bonded radii systematics in nitrides. In the Fall semester 1990 I will start graduate work in the Department of Mathematics, where I hope to earn a second Master's degree in Applied Mathematics.

A handwritten signature in cursive script, reading "Lewis Allen Buterakos". The signature is fluid and elegant, with a large, sweeping initial 'L'.