

## Effects of Covalency on Average Interatomic Distances in Germanates

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**Summary** For oxides containing tetrahedral germanium, a correlation exists between the average tetrahedral Ge-O distance and the average electronegativity of the cations surrounding the oxygen ions.

In derivations of effective ionic radii, it had been assumed<sup>1</sup> (i) that the effect of covalency in the shortening of M-X bonds is comparable in all M-F or M-O bonds, and (ii) that average cation-anion distances over all similar polyhedra in one structure are constant. The effects of covalency† were ignored in these assumptions and in the averaging over all possible structures containing M-O or M-F polyhedra. This procedure also ignores the so-called inductive effects of other cations in the structure.<sup>2-4</sup> Noll<sup>2</sup> showed for 13 silicate structures that individual Si-O(→M) distances differ from Si-O(→Si) distances and depend on the electronegativity of M. In silicates the electronegativity of M is generally less than that of Si so that electrons are donated to the Si-O(→M) bond, increasing its covalency and shortening the bond. Analysis of many accurately

interatomic distances. Here, we analyse the relationship between the *average* tetrahedral Ge-O distance in 14 germanate structures and the *average* electronegativity of the cations surrounding the oxygen ions.

Interatomic distances in oxide and fluoride structures<sup>1</sup> depend on the anion co-ordination, and an analysis of 46 three-dimensionally refined silicate structures<sup>6</sup> showed that a similar variation with oxygen co-ordination occurs in silicates. In order to separate the effects of anion co-ordination on interatomic distance from the effects of electronegativity of cations other than Ge<sup>4+</sup>, we have subtracted the appropriate anion radii from the interatomic distances according to the procedure in ref. 1. The Figure shows a plot of effective ionic radii *vs.* average electronegativity for 14 accurately refined germanates. We have used average electronegativities of all the cations in order to take the relative number of ions of differing electronegativity into account, for a compound M<sub>x</sub>T<sub>y</sub>O<sub>z</sub>, mean electronegativity is given by equation 1. The electronegativity

$$\bar{\chi} = \frac{x \cdot \chi_m + y \cdot \chi_t}{x + y} \quad (1)$$

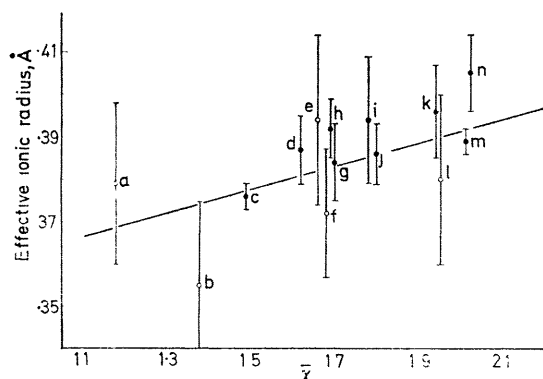


FIGURE. Effective ionic radius of  $(\text{Ge}^{\text{IV}})^{4+}$  *vs.* average electronegativity of cations surrounding oxygen. Vertical bars represent *e.s.d.* quoted by authors. Electronegativity values were taken from ref. 8. ● Estimated to be possibly more accurate.

refined silicate structures showed<sup>5-7</sup> that the electronegativity of the M ions greatly influences the individual

values used in calculating  $\bar{\chi}$  are those of Allred<sup>8</sup> and Batsonov.<sup>9</sup> Only those structure refinements with an *e.s.d.* ( $\sigma$ ) of  $\leq 0.02$  Å were used in the plot. Although the *e.s.d.*'s of many distances are quite large, it is apparent that the germanium (iv)<sup>4+</sup> radii (or in effect the interatomic distance corrected for anion co-ordination) increase as the average electronegativity of the other ions bonded to oxygen increases. A least-squares fit of a linear plot with each point weighted by  $1/\sigma$  resulted in  $r_{\text{Ge}} = 0.030 \bar{\chi} + 0.333$  with a standard deviation between  $r_{\text{obs}}$  and  $r_{\text{calc}}$  of  $\pm 0.010$  Å.

A decrease in average interatomic distances in tetrahedral oxy-ions may be caused by at least two factors. The first, a shortening associated with the decrease in oxygen co-ordination, is perhaps caused by an increase in *s*-character of the T-O bond.<sup>6,10</sup>

The second type of bond shortening is associated with a decrease in average electronegativity of the "other" ions in the structure. This shortening could be associated with increased  $\pi$  bond character. However, because this shortening effect also occurs in the tetrahedral borates and there can be no  $\pi$  bonds in tetrahedral borates (assuming

TABLE 1  
Interatomic distances and average electronegativities in germanates containing (Ge<sup>IV</sup>)<sup>4+</sup>\*

Compound	R, %	$\bar{\chi}$		(Ge-O) <sub>av</sub> - r(O <sup>2-</sup> )	r <sub>Ge</sub>	Ref.
		A	B			
Li <sub>4</sub> GeO <sub>4</sub> .. .. .	7.4	1.18	1.20	1.769 ± 0.019 - 1.390	0.379	a
Na <sub>2</sub> ZnGeO <sub>4</sub> .. .. .	15.5	1.38	1.35	1.735 ± 0.020 - 1.380	0.355	b
Mg <sub>28</sub> Ge <sub>10</sub> O <sub>48</sub> .. .. .	4.4	1.49	1.41	1.762 ± 0.003 - 1.386	0.376	c
Er <sub>7</sub> Ge <sub>3</sub> O <sub>7</sub> .. .. .	5.6	1.62	1.60	1.748 ± 0.008 - 1.361	0.387	d
LiNaGe <sub>4</sub> O <sub>9</sub> .. .. .	8.6	1.66	1.65	1.758 ± 0.020 - 1.364	0.394	e
Na <sub>4</sub> Ge <sub>9</sub> O <sub>20</sub> .. .. .	3.5	1.68	1.67	1.740 ± 0.015 - 1.368	0.372	f
Na <sub>9</sub> Sn <sub>4</sub> Ge <sub>10</sub> O <sub>30</sub> (OH) <sub>4</sub> .. .. .	4.9	1.70	1.69	1.752 ± 0.009 - 1.368	0.384	g
Mn <sub>2</sub> GeO <sub>4</sub> .. .. .	5.7	1.70	1.60	1.772 ± 0.007 - 1.380	0.392	h
MnGeO <sub>3</sub> .. .. .	8.0	1.78	1.70	1.757 ± 0.015 - 1.363	0.394	i
Mn <sub>3</sub> Fe <sub>3</sub> Ge <sub>3</sub> O <sub>12</sub> .. .. .	7.0	1.80	1.75	1.766 ± 0.007 - 1.380	0.386	j
CoGeO <sub>3</sub> .. .. .	9.2	1.94	1.90	1.759 ± 0.011 - 1.363	0.396	k
CuGeO <sub>3</sub> .. .. .	11.0	1.95	2.00	1.747 ± 0.020 - 1.367	0.380	l
GeO <sub>2</sub> .. .. .	1.9	2.01	2.00	1.739 ± 0.003 - 1.350	0.389	m
Na <sub>2</sub> GeO <sub>3</sub> ·6H <sub>2</sub> O .. .. .	8.5	2.02	2.01	1.768 ± 0.009 - 1.362	0.405	n

\*R = conventional R factor.  $\bar{\chi}_A$  = average electronegativities calculated from ref. 8.  $\bar{\chi}_B$  = average electronegativities calculated from ref. 9. r(O<sup>2-</sup>) = "effective ionic" radius of oxygen in a particular co-ordination (see ref. 1). r<sub>Ge</sub> = effective ionic radius of (Ge<sup>IV</sup>)<sup>4+</sup>.

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sp<sup>3</sup> hybridation on B), at least part of the reduction in bond

distance observed must arise from increased covalent character of the σ bond.

TABLE 2

Effect of average electronegativity of cations on the average interatomic distance in tetrahedral oxy-ions

T-O	Number of data points	Slope (m), <sup>a</sup> Å/electronegativity units	% Change in avg. interatomic distances for Δ $\bar{\chi}$ = 1 ΔR/[r(T) + r(O <sup>II</sup> ) <sup>2-</sup> ] <sup>b</sup>
B <sup>3+</sup> -O	23	0.03	2.2
Si <sup>4+</sup> -O	66	0.02	1.2
Ge <sup>4+</sup> -O	14	0.03	1.7
P <sup>5+</sup> -O	45	0.02	1.3
As <sup>5+</sup> -O	15	0.03	1.8
V <sup>5+</sup> -O	13	0.06	3.5
S <sup>6+</sup> -O	33	0.04	2.7
Se <sup>6+</sup> -O	6	0.07	4.2
Cr <sup>6+</sup> -O	11	0.03	1.8
Mo <sup>6+</sup> -O	13	0.03	1.7

<sup>a</sup> Slope determined by a least-squares fit of the data according to r(T) = m $\bar{\chi}$  + b.

<sup>b</sup> r(T) and r(O<sup>II</sup>)<sup>2-</sup> were taken from ref. 1.

Plots similar to the one shown in the Figure were made for the tetrahedral ions B<sup>3+</sup>, Si<sup>4+</sup>, P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup>, S<sup>6+</sup>, Se<sup>6+</sup>, Cr<sup>6+</sup>, and Mo<sup>6+</sup>. Table 2 shows that the variations in average interatomic distances (for Δ $\bar{\chi}$  = 1) depend on the nature of the tetrahedral ion and can be as much as 0.02—0.07 Å. Thus, interatomic distances in tetrahedral oxy-ions depend on both the number and electronegativity of the cations surrounding the oxygen ions. Decreases of average interatomic distances by as much as 0.03—0.04 Å can occur when highly electronegative ions such as Cu<sup>2+</sup> or Pb<sup>2+</sup> are replaced by highly electropositive ions such as Ca<sup>2+</sup> or Ba<sup>2+</sup> or when distances in hydrates are compared with those in anhydrous compounds. These covalency effects in tetrahedral oxy-ions are now being studied further.

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† In using the term covalency, we refer to electron density being shared by atoms regardless of bond type. Thus, we include the effect of both σ bonding, increasing in strength in the series LiF, BeO, BN, C and MgSe, BeSe, ZnSe, CdSe and d-p π bonding which presumably exists in the tetrahedral oxy-ions VO<sub>4</sub><sup>3-</sup>, MoO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, etc.

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