

π Bonding and Delocalization Effects in SiO₂ Polymorphs*

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The bond polarizability in SiO₂ polymorphs increases as the Si-O-Si bond angle increases and as the density decreases. This increase and systematic variations in other properties are due to π bonding between Si and O. Delocalization of π electrons in Si-O ring configurations and bond strain determine the properties of polymorphs of density under 2.33 g cm⁻³; they are also responsible for the pressure and irradiation behavior of SiO₂.

The structure of SiO₂ polymorphs is based on tetrahedral (4:2) coordination of Si and O atoms, the exception being stishovite with octahedral (6:3) coordination.¹ The difference in coordination is associated with a difference in molar refraction,^{2,3} but, within the tetrahedral coordination, variation in the refractive index has simply been attributed to variation in density. However, it has recently been indicated by the author that the molar refraction exhibits a systematic variation, reflecting differences in the Si-O bond.⁴ It is shown here that the bond polarizability exhibits an even more significant variation among SiO₂ polymorphs including stishovite and that this variation is related to the extent of π bonding between Si and O.

Since the Si-O bond is substantially covalent, calculation of ionic polarizabilities is not warranted. It has already been found that the use of bond, rather than atomic, polarizabilities gives consistent results for organosilicon compounds.⁵ Therefore, the polarizability of the Si-O bond, α_b , is used in this work. This is determined by dividing the molecular polarizability α_m by the coordination number of silicon; in turn, α_m is calculated from the Lorenz-Lorentz equation,⁶

$$R_M \equiv \frac{n^2 - 1}{n^2 + 2} V_M = \frac{4}{3} \pi N \alpha_m, \quad (1)$$

where R_M is the molar refraction, n is the refractive index (at 589 nm in this work), V_M is the molar volume, and N is Avogadro's number.

The bond polarizabilities and some other pertinent properties of SiO₂ polymorphs are listed in Table I. It can be seen that the greatest change in bond length and bond polarizability is associated with the change in coordination from octahedral to tetrahedral (from stishovite to coesite). This change in bond polarizability is more significant than the change in molar refraction, as demonstrated by the extrapolated values for stishovite; these were obtained from linear extrapolation

of R_M and α_b versus density from vitreous SiO₂ to coesite. It is not immediately obvious why a decrease in bond length is associated with an increase in bond polarizability. It is known that, except for a few important cases (e.g., C-C, C-O bonds), the bond polarizability usually increases with bond length.⁸

From coesite to α -cristobalite, the general trend is that, with increasing structural symmetry (from monoclinic to pseudocubic), the bond length decreases very slightly, but the Si-O-Si bond angle increases significantly, resulting in a decrease in density. Accompanying this change are increases in bond polarizability, Si-O valence vibration frequency, and directionality ratio.

The change in various properties from stishovite to α -cristobalite can be attributed to increasing $d\pi$ - $p\pi$ bonding between silicon and oxygen. This π bonding arises from the overlap of (the originally empty) Si $3d$ orbitals with the O $2p$ orbital containing the lone pair electron.⁹ Recently, x-ray spectroscopy of silicates¹⁰ has provided direct evidence of π levels.

In stishovite, the atomic arrangement is unfavorable for $d\pi$ - $p\pi$ overlap; hence, the bond length is as expected on the basis of the mixed covalent (σ bond) and ionic bonding. In tetrahedral coordination, the $d\pi$ - $p\pi$ overlap can develop, but its extent depends very much on the Si-O-Si bond angle; the overlap becomes more favorable as the angle becomes larger. Thus, π bonding increases with the Si-O-Si angle, resulting in increased bond strength (bond order) and in Si-O valence vibration frequency, as well as in decreased bond length. Meanwhile, the ionic component of the bond decreases; this is reflected in the increase of the directionality ratio. Increasing π bonding is also responsible for the observed¹¹ increasing etch rate in HF from stishovite to vitreous silica.

The increase in bond polarizability with π bond-

TABLE I. Bond polarizabilities and some other bond-related properties of SiO₂ polymorphs. The headings β , ν , and r stand for the Si-O-Si bond angle, Si-O valence vibration frequency, and the directionality ratio,^a in this order. Except when indicated, data were taken from Ref. 1. For birefringent crystals, the mean refractive index was determined as $n = (n_x^2 n_y^2)^{1/3}$. For stishovite, the extrapolated values (see text) are given in parentheses.

Polymorph	Bond length, nm	Density, g cm ⁻³	n	R _M , cm ³ mole ⁻¹	α_b , 10 ⁻²⁵ cm ³	β	ν , cm ⁻¹	r
Stishovite	0.177		1.830			- ^b	885 ^d	- ^b
natural		4.03		6.54	4.32			
synthetic		4.35		6.06 (6.25)	4.00 (5.44)			
Coesite	0.160 - 0.163 ^c		1.596			~139° ^c	1077 ^d	0.163 ^d
natural		2.87		7.12	7.05			
synthetic		2.92		7.01	6.94			
α -Quartz	0.1603 and 0.1611 ^e	2.65	1.549	7.21	7.13	143.9° ^e	1078 ^d	0.178 ^d
Keatite		2.50	1.519	7.29	7.23			
α -Cristobalite	0.1601 and 0.1608 ^f	2.33	1.485	7.39	7.32	146.8° ^f	1095 ^g	0.199 ^g
α -Tridymite		2.27	1.473	7.42	7.35		1106 ^g	0.188 ^g
Vitreous	0.160	2.20	1.458	7.45	7.38	150° ^h	1098 ^d	0.182 ^d
Melanophlogite		1.99 ⁱ	1.425	7.71	7.64			

^aThis measures the ratio of noncentral (directed) to central (undirected) binding forces [J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970)]; its value was determined by k_1/k_2 , where k_1 and k_2 are the force constants of Si-O-Si bending and Si-O valence vibrations, respectively.

^bBecause of the 6:3 coordination in stishovite, these values are meaningless in the context of our discussion; therefore, they are not shown.

^cT. Zoltai and M. J. Buerger, Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem. **111**, 129 (1959); the bond lengths represent the extremes of four values.

^dFrom Ref. 3.

^eR. A. Young and B. Post, Acta Crystallogr. **15**, 337 (1962).

^fW. A. Dollase, Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem. **121**, 369 (1962).

^gT. Rey, Z. Kristallogr. Kristallgeometrie, Kristallphys., Kristallchem. **123**, 263 (1966).

^hRepresents a mean value of some unspecified distribution; from Ref. 7.

ⁱFrom Ref. 8.

ing is well known from the examples of the C-C and C-O bonds.⁸ The analogy between Si-O and C-O bonds is especially close since the ratio of the relative increase in α_b to the relative decrease in bond length, i.e., $(\Delta\alpha_b/\alpha_b)/(\Delta l/l)$, where l is the bond length, can be calculated (for the C-O bond from values given in Ref. 8) as -9.3 for both cases. Based on this similarity, the bond order in α -cristobalite can be estimated as 1.47 by taking the bond order in stishovite as unity. Molecular orbital considerations imply a value of 1.5, assuming full participation of the lone pair electrons of the oxygen in the π bond.⁴

The above described correlation between bond polarizability and other properties does not hold when the density is less than 2.33 g cm⁻³ (corresponding to α -cristobalite); in this density range there appears to be a trend of increasing

bond polarizability with decreasing valence vibration frequency and directionality ratio. The behavior is similar to that exhibited by ring structures derived from benzene: As the number of associated rings increases from one (benzene) through two (naphthalene) and three (anthracene) to infinity (graphite), the bond length increases from 0.1397 to 0.1420 nm and the bond order decreases from 1.50 to 1.35. However, the bond polarizability increases from 10.9×10^{-25} cm³ (benzene) through 11.7×10^{-25} cm³ (anthracene) to 15×10^{-25} cm³ (graphite).¹² This is evidently due to increasing delocalization of π electrons that reaches a maximum in graphite.

Delocalization of π electrons in benzene-based structures is a consequence of the arrangement of C atoms in six-member rings. It is known that Si and O atoms also form various cyclic com-

pounds involving three to nine Si atoms.¹⁴ The structures of coesite and α -cristobalite are based on four- and six-membered rings, respectively. In quartz the rings are distorted so that Si and O atoms form a helix along the c axis. The fact that the average Si-O bond polarizability is higher in cyclic dimethyl siloxanes (7.04×10^{-25} cm³ as calculated from data in Ref. 14) than in the corresponding linear siloxanes (6.80×10^{-25} cm³) indicates non-negligible delocalization in Si-O rings.

Delocalization of π electrons in Si-O rings increases with ring size, but so does the bond strain.¹⁵ Therefore, in equilibrium, the energy gained by delocalization is balanced by the energy required for straining the bonds. Increasing structural symmetry of SiO₂ polymorphs favors larger SiO_{4/2} rings; the increased energy content (standard enthalpies of formation are -217.7 and -215.9 kcal mole⁻¹ for α -quartz and vitreous SiO₂, respectively) apparently overcomes the bond strain, so that π bonding and delocalization increase from coesite to α -cristobalite.

The extent of bond strain is very limited in a perfect crystal, but disorder and impurity effects facilitate the accommodation of larger bond strain. These effects play an increasingly important role as we go from α -cristobalite to melanophlogite. It is known, for instance, that tridymite cannot be obtained without some impurity. Also, both tridymite and α -cristobalite have a great tendency toward disordered crystal structures.¹ There is, of course, no long-range order in vitreous and other noncrystalline silicas; this is reflected in the characterization of the Si-O-Si bond angle by a distribution around a mean instead of a singular value. This results in a distribution of four- to eight-membered SiO_{4/2} rings in vitreous silica¹⁶ that cannot occur in crystalline SiO₂.

There are apparently many possible structural conformations having very nearly the same energy; hence, the properties of SiO₂ polymorphs in the density range of about 2.33 to 2.20 g cm⁻³ exhibit an almost continuous overlap. This can be illustrated by the range of molar refraction values of tridymite, 7.386-7.478 cm³ mole⁻¹ (calculated from Table 4 in Ref. 1), and of vitreous silica, 7.40-7.48 cm³ mole⁻¹ (taken from various reported values).

The effect of bond strain reaches its maximum at melanophlogite, the very existence of which is due to pigment inclusions.¹⁷ With these inclu-

sions, extremely large rings and associated bond strain can apparently be accommodated, resulting in a high value of bond polarizability. This structure is rather unstable and, when the bond strain can no longer be maintained, it collapses. This explains the peculiar observation¹⁷ that grinding at room temperature is sufficient to convert melanophlogite to quartz.

In the density range of 2.20-2.33 g cm⁻³, significant delocalization of π electrons can take place if the structure allows some bond strain. As a result, the bond polarizability increases, but the bond order decreases. Hence, the force constant (valence vibration frequency) and directionality ratio also decrease. Effects related to the conformation of various structural groups (rings, chains, and helices) are very important in phenomena occurring in SiO₂ as a result of irradiation and pressure. The fundamental trend in these conformational changes is to maximize π bonding with minimum bond strain. In this respect, SiO₂ exhibits a rather unusual behavior that can be understood if we consider silica more as a fully cross-linked siloxane-type polymer than as an ionic or covalent crystal or random network. This behavior is largely due to the flexibility of the Si-O-Si bond angle (quite in contrast with the rigidity of the O-Si-O angle).

Enhanced π bonding and delocalization of π electrons in the distorted rings along the c axis of α -quartz may also be responsible for the striking anisotropy in its etching¹⁸ and electronic conduction¹⁹ behavior.

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¹For a recent review see O. W. Flörke, *Fortschr. Mineral.* **44**, 181 (1967).

²F. Dacheille and R. Roy, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.* **111**, 462 (1959).

³J. Zarzycki, in *Physics of Non-Crystalline Solids*, edited by J. A. Prins (North-Holland, Amsterdam, 1965), p. 525.

⁴A. G. Revesz, *J. Non-Cryst. Solids* **4**, 347 (1970).

⁵E. L. Warrick, *J. Chem. Soc.*, London **68**, 2455 (1946).

⁶Equation (1) usually holds well for dense gases and liquids, but frequently underestimates α_m and hence α_b for covalent solids. [J. C. Phillips, *Covalent Bonding in Crystals, Molecules, and Polymers* (University of Chicago Press, Chicago, 1969), pp. 7-14]. However, this is not the case for the Si-O bond since the bond polarizabilities for solid SiO₂ polymorphs (see Table I) are higher than those for liquid siloxanes, about 6.93×10^{-25} cm³ (Ref. 5), indicating that the interactions between Si-O bonds in these solids and liquids are comparable.

⁷L. Cartz, Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem. **120**, 241 (1964).

⁸B. J. Skinner and D. E. Appleman, Amer. Mineral. **48**, 854 (1963).

⁹K. G. Denbigh, Trans. Faraday Soc. **36**, 936 (1940).

¹⁰For a review of $d\pi-p\pi$ bonding, see K. A. R. Mitchell, Chem. Rev. **69**, 157 (1969).

¹¹C. G. Dodd and G. L. Glen, J. Amer. Ceram. Soc. **53**, 322 (1970).

¹²J. J. Fahey, Amer. Mineral. **49**, 1643 (1964).

¹³Except for graphite, the bond polarizabilities have been calculated from data in standard tables. For graphite $n=2.73$ was used; this value is for light polar-

ized in the plane of the carbon rings [D. L. Greenaway *et al.*, Phys. Rev. **178**, 1340 (1969)]. Bond-order values were taken from L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N. Y., 1960), pp. 234-239.

¹⁴W. Noll, *Chemistry and Technology of Silicones* (Academic, New York, 1968), Chap. 6.

¹⁵D. P. Craig and N. L. Paddock, J. Chem. Soc. **1962**, 4118.

¹⁶O. Mugge, as quoted in W. C. Levengood, J. Appl. Phys. **30**, 378 (1959).

¹⁷S. Okabe, T. Tsumari, and T. Tabato, J. Appl. Phys. **40**, 2894 (1969).

Electronic Density of States of Amorphous Si and Ge

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The density of states of the valence and conduction bands of Si and Ge are discussed using a simple tight-binding Hamiltonian. It is shown that certain features of the density of states for the case of the diamond structure are related to the short-range order and hence should be retained in the amorphous state while others depend on long-range order and are expected to disappear.

Much recent experimental effort has been devoted to the determination of the electronic density of states of amorphous semiconductors, particularly Ge^{1,2} and Si,^{3,4} and the results so far obtained have excited a good deal of theoretical speculation on the subject.⁵⁻⁷ An accurate comprehensive theory for the electronic properties of these solids is still lacking^{8,9} and is likely to remain so for some time. However it has recently been shown^{10,11} that the problem is not wholly intractable if a simple Hamiltonian of the tight-binding type is used—in particular, it can be shown that for such a Hamiltonian there is a gap in the electronic density of states for *any* structure with tetrahedral coordination of nearest neighbors. This dispels some, if not all,¹² of the mystery surrounding the observation¹⁻⁴ of such a gap in the amorphous state. In this Letter the same Hamiltonian is used to give a discussion of the shape of the density of states for crystalline and amorphous semiconductors which hinges on a question that has long been of interest in this area but has hitherto been almost entirely unresolved. *Which features of the crystalline density of states are due to the long-range order of the structure and which are due only to the short-range order?* Only the latter are expected to be retained in the amorphous structure since this

has essentially the same short-range order as the crystal but without the accompanying long-range order. Our conclusions appear to be consistent with the evidence available at present and we suggest a measurement which should provide a critical test of the model.

Our Hamiltonian^{10,11} acts on a set of basic functions $|\varphi_{ij}\rangle$ which are the “ sp^3 ” hybridized orbitals that can be formed at each atomic site. The subscript i refers to the atom and j to the bond. Bonding and antibonding states can be formed with the four nearest neighbors of each atom that lie at the corners of a tetrahedron. The Hamiltonian contains two parameters V_1 and V_2 :

$$H = V_1 \sum_i |\varphi_{ij}\rangle \langle \varphi_{ij'}| + V_2 \sum_j |\varphi_{ij}\rangle \langle \varphi_{i'j}|; \quad (1)$$

these are, respectively, the matrix element between orbitals associated with the same atom (and different bonds) and the matrix element between orbitals associated with the same bond (and different atoms). Such a simple Hamiltonian cannot be expected to give a very accurate description of Si and Ge but it does provide quite a good qualitative description of the valence bands of these semiconductors in the crystalline state.^{11,13} Figure 1 compares the density of states calculated from this Hamiltonian for the diamond struc-