

SHORT COMMUNICATIONS

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Interpretation of some structures of SiO₂ by assumptions on the electron spatial correlation. By K. SCHUBERT, *Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestraße 92, 7000 Stuttgart, Germany*

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Abstract

Some structural phenomena in phases of SiO₂, not understood so far, may be interpreted if an appropriate lattice-like averaged spatial correlation [Schubert (1990). *Bonding Types of Two-Component Phases I*. Stuttgart: Max-Planck-Institut für Metallforschung] of the electrons is assumed. In high-cristobalite the valence electrons of Si are mainly in a face-centred cubic correlation (b_F). Since the atomic structure is very loosely packed, the b_F correlation is only partly occupied and the missing electrons fill some octahedral interstices of b_F (b_F -correlation). This assumption explains the shift of O atoms from the ideal positions in high-cristobalite, the shear homeotypism of high-tridymite to high-cristobalite, the strong change of the axial ratio of quartz as compared with that of high-tridymite, and several additional phenomena.

The oligotypic compound SiO₂ contains six phases, stable at certain thermodynamic states, and numerous metastable phases, having no stability range (Rochow, 1973; Wriedt, 1990). The structures of the phases have partly been interpreted by assumptions on the spatial correlation of the electrons (Schubert, 1988). This kind of interpretation provides an intuitive access to the bonding *via* crystal-chemical rules and may be preferred to a more conventional explanation by electron-pair bonding. Since the electron-pair bonding model does not take into account the core electrons explicitly, its fundamental assumptions are different from the present ones, so that this model cannot be examined in this note. In the following, the electron correlation interpretation of SiO₂ phases is improved and extended.

SiO₂. h_2 , 1743–1978 K [*F2-4*; high-cristobalite; *Strukturbericht*, **1**, 169 (SB1.169); *Structure Reports*, **41**, 104 (SR41.104)] is the second stable high-temperature phase (h_2) of SiO₂. SB1.169 describes a zero approximation of the structure: a cubic face-centred cell (F) contains in its primitive part two Si and four O atoms so that *F2-4* is a convenient symbol (Schubert, 1964, p. 87) for the calculation of the electron numbers per cell. A drawing of the SR1.169 structure of h_2 may be found in Schubert (1964, p. 200); it is described according to Lima-de-Faria, Hellner, Liebau, Makovicky & Parthé (1990) by Si ^{$F2O_2^{[2]}$} where *F2* is the diamond structure and [2] indicates the number of Si

atoms coordinated to O. After Wright & Leadbetter (1975) (SR41.104) the O atoms do not lie exactly midway between two Si atoms but are slightly shifted perpendicularly to the Si—Si line. This remarkable fact should be explained by the bonding.

The bonding type as derived by the method of Schubert (1983, 1986, 1990) is described by $a(32, 160) = (7 \cdot 13 \text{ \AA}) = b_F(2) = g_F(4)$. Here a is the crystal cell matrix; (32, 160) are the numbers of valence electrons (Si $3sp$) and of core electrons (Si $2sp + O 2sp$) per a ; b_F is the valence electron correlation cell matrix of the $F1$ type; it is multiplied by the commensurability matrix $(2) = (2, 0, 0; 0, 2, 0; 0, 0, 2)$ to equal a ; g_F is the core electron correlation cell matrix also of the $F1$ type and is multiplied with the commensurability (4). The lattice (belonging to) b_F is a sublattice of g_F and the lattice g_F has enough sites to accept all electrons. This 'collective' property is energetically favourable, it causes the spin compensation known from the electron-pair bonding model. However, the acceptability of this '*FF2*' proposal must be judged from the rules of Schubert (1986, 1990) and from the compatibility with the electron distances collected in Schubert (1990). It is easily seen that the electron distances $d_b = 2.5 \text{ \AA}$ (and $d_r = 1.25 \text{ \AA}$) are too long. This is caused by the loose packing of the structure failing to give support to all sites of the b correlation. A means to correct for this is to leave unfavourable b_F sites unoccupied and to fill instead an equal number of favourable 'insertion' sites (b_F), *i.e.* b_F is partly filled with + spins and some octahedral holes of b_F are filled with + spins (inhomogeneous correlation). This phenomenon in SiO₂. h_2 implies no deviation from Hund's rule attributing four + spins to Si. The amount of insertion may be assumed to be somewhat dependent on the thermodynamic state. Geometrically it may be seen that the insertion in b_F is frequently in collision with the O sites of the SB1.169 structure, *i.e.* an O site and an insertion site frequently coincide. This instability may be removed by a structure isotypic to the SR41.104 structure. The g_F correlation does not favour spin compensation, it must therefore contain a tendency to be deformed as will be seen for h_2m and h_1 .

The metastable SiO₂. h_2m (*T4-8*; low-cristobalite; SB3.25,299) is a contracted homeotype of h_2 [see drawing in Schubert (1964, p. 200)]. This observation fits the assumption of an increased amount of insertion. Also in the next phase (Wriedt, 1990) this argument holds.

SiO_2, h_1 , 1143–1743 K ($H4\cdot8$; high-tridymite; SB1.203, drawing SB1.171) is a stacking homeotype of h_2 and its bonding type may be derived (Schubert, 1986) as $a(16, 80) = H5\cdot03$; $8\cdot22 \text{ \AA} = b_{FH}(2; 4\cdot5/3) = g_{FH}(4; 9/3)$. Here H in the numerical value of a indicates a hexagonal coordinate system; b_{FH} is the valence electron correlation cell of the $F1$ type in hexagonal aspect as noted by the suffix H , and additionally compressed (\sim) in the direction of the hexagonal axis; b_{FH} is multiplied by a commensurability matrix in abbreviated notation (Schubert, 1986); g_{FH} is analogous to b_{FH} . The bonding type is closely homeotypic to the bonding type of h_2 . The compression of F apparently improves the spin compensation in g . When the $(111)_F$ planes of g are closer together and consecutive layers are alternatively occupied by $+$ and $-$ spins, compensation is provided. Such a model may be approximated by b_{FH} . In the case of h_1 the contraction has attained the commensurability $a = g_{FH}(4; 9/3)$ and, as shown in Schubert (1984), the matrix element $(g^{-1}a)_{33} = 3$ in the above bonding type favours the stacking sequence of the tridymite type. The observation that h_1 has nearly the ideal value of the axial ratio may be explained by the fact that the compression of b_F sites decreases the axial ratio while the higher site number increases it. The insertion of additional sites in b has the consequence that the b sites are not all occupied. Therefore at lower temperatures structures must be expected in which all b sites are occupied (Schubert, 1986). Numerous metastable homeotypes (Wriedt, 1990) of tridymite are still to be considered for interpretation. Also, at this point, the existence of the hexagonal carbon phase $C.hp_1$ (ZnO , $H2\cdot2$, SR32.147) should be mentioned.

SiO_2, r_2 , 848–1143 K ($H3\cdot6$; high-quartz; SB1.166, SR27.674) has been said to be a submicroscopic twinning of low quartz (SR27.674) and shows a cell $a = H5\cdot03$; $5\cdot45 \text{ \AA}$. It must be assumed for structural reasons to be closely homeodesmic to r_1 . The difference between h_1 and r_1 may therefore be considered for r_1 .

SiO_2, r_1 , 0–848 K ($H3\cdot6$; low-quartz; SB3.21, SR30.420, 42.393, drawing Schubert, 1964, p. 200) has an $\text{Si}^{(4)}\text{O}_2^{(2)}$ structure like h_2 and h_1 but the support number (Schubert, 1964, p. 19) in the direction $[111]_{h_2}$ for the Si atoms does not alternate between one and three, as in h_2 and h_1 , but is invariably two. The bonding type proposal for r_1 shows that full occupation of b is attained: $a(12, 60) = H4\cdot91$; $5\cdot40 \text{ \AA} = B_{FH}(2; 3/3) = g_{FH}(4; 6/3)$. The contraction of b_{FH} is essentially as large as in h_1 . This fact indicates that b_{FH} is no longer a good description of b . If the hexagonal b_1, b_2 and g_1, g_2 nets lying parallel to $(a_1, a_2)_{r_1}$ are stacked in the a_2 direction with support number two then a favourable homogeneous spin ordering may be attained by attributing different spins to neighbouring g_1, g_2 layers. This correlation may be named b_{UH}, g_{UH} (Schubert, 1986, 1990), and the bonding type of r_1 may be written $a = b_{UH}(2; 3/2) = g_{UH}(4; 6/2)$. The b_{UH} correlation contains only one spin sign because of the collective property. The quartz structure is apparently transformed from the $H4\cdot8$ structure by the striving after full occupation of b .

Having so far discussed normal pressure phases, finally two high-pressure phases (p) should be considered, although their structures were determined in the metastable state (Wriedt, 1990). However, since both phases are prepared from r_1 without mineralizer the state during preparation will be a state of stability.

SiO_2, p_1 , 900 K, $> 3\cdot5 \text{ GPa}$ ($N8\cdot16$; coesite; SR23.340, drawing SR23.340) is a monoclinic face-centred high-pressure phase. Its $\text{SiO}_{4/2}$ tetrahedra form Si_4O_{12} rings in the a_1, a_2 plane, the rings are connected by common O atoms to chains in the a_2 direction and these chains are connected by common O atoms with four parallel neighbouring chains. The pseudo-hexagonal cell points to the bonding type: $a(64, 192, 192) = H7\cdot17$; $12\cdot38 \text{ \AA} = b_{UH}(3; 7/2) = g_{UH}(6; 14/2)$. b is slightly overoccupied which may be mitigated by a small increase of the matrix element from 7 to 7.1. The fitting of the r_1 bonding type in p_1 is a geometrical relation which might be formulated independently of the bonding type, but the conservation of the bonding type is an expression for the observation that p_1 may be formed directly by compression of r_1 (Wriedt, 1990). The g site number per atom is 10.7 for both the r_1 and the p_1 phase; therefore, the participation of $\text{O } 1s^2$ electrons in g may be a cause for the transformation $r_1 \rightarrow p_1$. Another possibility is the exactness of the matrix element 7 connected with a departure of stoichiometry; however, this was denied by Gibbs, Prewitt & Baldwin (1977).

SiO_2, p_2 , 1500 K, 14 GPa (TiO_2, r ; $T2\cdot4$; stishovite; SR27.675, drawing Schubert, 1964, p. 275) obeys the rule of Range (1976) that a pressure phase may be isotypic to a heavier quasi-homologic room-pressure phase because of the bonding contribution of the lower electrons in the heavier phase. The coordination is now $\text{Si}^{(6)}\text{O}_3^{(3)}$. To find the bonding type, it should be noted that the increase of pressure favours a C correlation: $a(8, 16, 32) = 4\cdot18$; $2\cdot67 \text{ \AA} = b_C(5^{1/2}; 1\cdot4) = g_C(20^{1/2}; 2\cdot85)$. Here C is the cubic primitive correlation. g is compatible with spin compensation while b follows Hund's rule. It appears that the $\text{Si } 1s^2$ electrons do not take part in the bonding. The g correlation is nearly fully occupied by b and g electrons. This does not mean that the electrons are uniformly distributed since only the narrow stripes of the spatial correlation far from the atomic core are of influence (Schubert, 1990, p. 11, Fig. 1).

The closely related bonding types found for various phases of SiO_2 represent numerogeometrical rules for these phases. The hypothesis that these rules have to do with the bonding type must be confirmed by a further analysis of similar rules in other compounds (see Schubert, 1990).

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