Polymorphism of Silica and Ice

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The polymorphism of both silica and ice is described by a new chemical relationship between the different crystalline structures (cristobalite, etc.). This relationship is given by the set of admissible screw axes of a tetrahedrally coordinated crystal. The various winding numbers correspond to commensurate cylindrical superstructures calculated from a nonlinear model for both oxygen bonds (SiO_2) and hydrogen bonds (H_2O). Glass, in this description, is a strongly incommensurate ("chaotic") modification of cristobalite.

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The microscopic origin of the chemical structure of insulators is, at present, understood for a few cases only. Elementary covalent semiconductors, for example, exhibit the diamond structure, which originates mainly from the sp^3-hybridized four valence electrons of each atom. The tetrahedral coordination of these crystals is not changed[1] if one adds oxygen to the bonds as in SiO_2. The oxygen ions play the role of "bridges" between the silicon ions by replacing the "bond charges" of silicon. Therefore, the tetrahedral topology and the pattern of lattice forces are similar in SiO_2 as compared to silicon. Nevertheless, in contrast to silicon, a surprising polymorphism is observed in silica, where, in addition to the diamondlike cristobalite, several other structures (tridymite, etc.) and various complex structures are observed.[1,2] The effective oxygen charge is between $-1e$ and $-2e$.[3] No microscopic explanation seems to exist for the polymorphism of the silica.

A remarkable analog of these properties is found in the polymorphism of ice.[1,4] Here the bridges are formed by hydrogen bonds while oxygen takes the place of the tetrahedral silicon. Thus, ice can be visualized as a crystal family with "anti"-SiO_2 structure. The electronic structure of H_2O is preformed in the liquid phase: "The molecule of water appears to be a somewhat deformed O^{2-} ion with two protons."[5]

In this paper we are going to show that the polymorphism of both silica and ice is due to the specific electronic structure of the oxygen and hydrogen bonds, respectively. Our starting point is the nonlinear electron-lattice coupling at the sites of oxygen (O^{2-}) ions which strongly determines the properties of oxides, in particular of ferroelectrics.[6] This coupling is well described by a double-well polarization potential with a negative harmonic and a repulsive fourth-order term. The potential stems from the configurational instability of the oxygen ions. This leads to nonbonding orbitals at the upper part of the oxygen valence bands ("lone pairs").[3] The lateral distortion of the Si—O—Si bond [Fig. 1(a)] induces a dipole moment at the oxygen lattice site *perpendicular* to the interconnecting line. The α phase of SiO_2 would be ferroelectric if the SiO_4 units had no tetrahedral symmetry.

A similar instability is known for the hydrogen bond in inorganic and organic systems where the proton below the transition temperature T_c sits in an asymmetric position in the bond, while above T_c it is in disordered "para" phase[7] [Fig. 1(b)]. In inorganic ferroelectrics like potassium dihydrogen phosphate (KDP) double-well potentials for both H and the PO_4 group describe the strong isotope effect upon deuteration.[8] The hydrogen bond in KDP is similar to that in ice since in both cases the "ice rule" is observed, i.e., a pairwise clustering of protons in the "ferro" phase. The difference of the hydrogen from the oxygen bond is the bond-stretching character of the double-well potential *parallel* to the O—H—O line. Since the double-well potential can provide a complete set of commensurate structural lattice transformations[9] one should look for the corresponding effect for the SiO_2

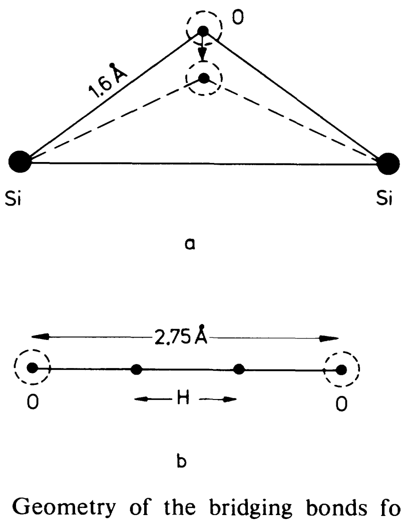

FIG. 1. Geometry of the bridging bonds for (a) SiO_2, where the bond angle varies between 140° and 180° for different materials and is strongly temperature dependent, and (b) H_2O, where the hydrogen ion occupies one of two equivalent positions.

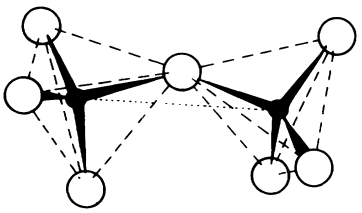

FIG. 2. Building blocks, dimer of two corner-linked SiO_4 tetrahedra, of the polymorphic structures: open circle, oxygen; solid circle, silicon.

and ice lattices.

The similarity between the oxygen and hydrogen bonds suggests a model Hamiltonian subsuming both cases: the silica and the ice family. The novel element in our model theory is the relation of polymorphism to a unique set of screw axes. The various "spiralities" are given by those cyclic rotations of the point group which are consistent with the crystal periodicity. It follows from standard group theory that only the winding numbers $N=1$, 2, 3, 4, and 6 are consistent with three-dimensional periodic structures. The relation of N to the screw axes in SiO_2 and ice becomes obvious if we map the real structure along the (111) direction (or the equivalent c axis) onto a cylinder. The "particles" of this mapping are dimers of corner-linked SiO_4 tetrahedra (Fig. 2). The transformation is a rotation R defolding the structure of highest symmetry, i.e., the "diamond" lattice, into a straight line on the cylinder (Fig. 3). It reads

$$\mathbf{R}_{111}\times(1,2,3)_{\text{diamond}}\rightarrow(1,2,3)_{\text{cylinder}}, \tag{1}$$

with $\mathbf{R}_{111}=(2\pi/3)(0,1,2)$ and (1,2,3) denoting a sequence of three "particles." The winding number $N=1$ corresponds to cristobalite or ice Ic. $N=2,3$, etc., reflect the increasing number of particles per unit cell for the other polymorphic structures (see Table I).

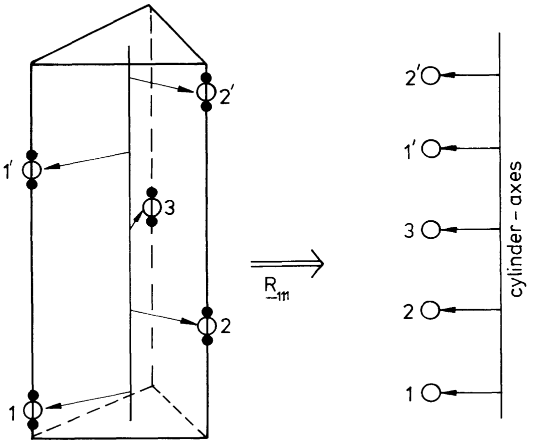

FIG. 3. The mapping of the diamond structure onto a straight line on a cylinder (see text).

The model Hamiltonian describes the particles of one single cylinder only. Their polarizability is given by the double-well potential. The interaction between particles generates short-range interatomic forces (Fig. 4). The long-range Coulomb forces are considered in terms of a local-field correction[10] replacing the bare *positive* harmonic electron-lattice coupling by an effective *negative* coupling, thus leading to a double-well potential. Here we focus on its symmetric part, while the asymmetric part may be described by an effective external pressure. This would not change the following results concerning the symmetry and metastability of the different static configurations. It should, however, be considered in a more quantitative treatment.

The Hamiltonian reads

$$H=\tfrac{1}{2}\sum_n(M\mathbf{u}_n^2+m_e\mathbf{v}_n^2)+V, \tag{2}$$

$$\begin{aligned}V=f'\sum_n\{u_n[u_n-u_{n-1}\cos(\phi_n-\phi_{n-1})]+u_{z,n}(u_{z,n}-u_{z,n-1})\}\\+f\sum_n\{v_n[v_n-v_{n-1}\cos(\phi_n-\phi_{n-1})]+v_{z,n}(v_{z,n}-v_{z,n-1})\}\\+\tfrac{1}{2}g_2\sum_n[(u_n-v_n)^2+(u_{z,n}-v_{z,n})^2]+\tfrac{1}{4}g_4\sum_n[(u_n-v_n)^2+(u_{z,n}-v_{z,n})^2]^2,\end{aligned} \tag{3}$$

with the cylindric coordinates (Fig. 4)

$$\mathbf{u}_n(u_n\cos\phi_n,\ u_n\sin\phi_n,\ u_{z,n}), \tag{4}$$

$$\mathbf{v}_n=(v_n\cos\phi_n,\ v_n\sin\phi_n,\ v_{z,n}), \tag{5}$$

$$\phi_n=2\pi n/N. \tag{6}$$

The potential, Eq. (3), implies the constraint that the core displacements $\mathbf{u}_n$ are in the same direction ϕ_n as the electronic-"shell" displacements $\mathbf{v}_n$. This seems to be a sufficient approximation for the following investigation.

The equilibrium configurations for the high-temperature β phases of the Hamiltonian (2) are given by

$$\frac{\partial H}{\partial u_n}=\frac{\partial H}{\partial v_n}=\frac{\partial H}{\partial u_{z,n}}=\frac{\partial H}{\partial v_{z,n}}=\frac{\partial H}{\partial\phi_n}=0. \tag{7}$$

The solutions of Eqs. (7) that are consistent with translational symmetry are summarized in Table I. They show a nearly complete classification of the different main crystal structures of silica and ice in terms

TABLE I. Tetrahedral SiO_2 and ice structures: parameter $b = f_{\text{eff}}/g_2$. There are in the cases marked with asterisks additional rotations of particles.

Ice (density)	Silica (density)	Number of units	Spirality N	Energy	Displacement vector
I*c* (0.92)	Cristobalite (2.27)	2	1	-1	$(\cos 2\pi n,\ 0,\ -r_1 \cos 2\pi n)$
I*h* (0.92)	Tridymite (2.26)	4	2	$-(1+4b)^2$	$(\cos \pi n,\ 0,\ -r_2 \cos 2\pi n)$
· · ·	Quartz (2.65)	6	3	$-2(1+3b)^2/3$	$(\cos(2\pi n/3),\ \sin(2\pi n/3),\ 0)^*$
III IV (1.16)	Keatite (2.50)	3×4	6	$-2(1+b)^2/3$	$(\cos(\pi n/3),\ \sin(\pi n/3), 0)^*$
· · ·	Coesite (2.90)	2×8			
· · ·	Glass (2.20)	Irregular	· · ·		

of spiralites, i.e., of winding numbers N of the model. Some comments may be in order: (i) The energy per cell of the various static structures depends on the effective intercell coupling, $f_{\text{eff}}^{-1} = f^{-1} + (f')^{-1}$. The different metastable solutions are stable against small ion displacements ("phonon" stability). (ii) For ice no phase with $N = 3$ (quartz) exists. This structure is probably not stable because it requires a symmetric position of every third proton along an O-H-O chain with a high activation energy.[1] (iii) The increase of density with winding number N indicates the corresponding increase of second-nearest-neighbor forces. In a refined model with interaction between cylinders they should be considered. Stishovite exhibits an octahedral coordination (rutile structure) probably due to a stability limit at higher densities.[1] (iv) The low-temperature α phases are described, within our model, by solutions with different radii for the model cylinder. For example, the sixfold rotational symmetry of quartz along the (0001) direction is reduced to a threefold rotational symmetry during a $\beta \rightarrow \alpha$ transition[11] (Fig. 5). Thus, the $\alpha \rightarrow \beta$ transition of silica corresponds to an antiferrodistortive phase transition related to a softening of the tilt angle between SiO_4 units.[12] (v) Consideration of attractive intercell forces exhibits the possibility of a commensurate-incommensurate transition between the α and β phases. (Cf. the similar situation in K_2SeO_4.) An intermediate phase was predicted for quartz[13] and recently has been observed.[14]

Our approach to the polymorphism of silica and ice is different from both the standard group-subgroup relations for structures that are topologically equivalent,[15] and the well-known polytypism in these structures.[11] In case of the polymorphism the different though topologically equivalent members form a "ring" of aristotypes. It is mathematically given by those spiralities of the tetrahedral coordination which are consistent with translational symmetry. The ring can be visualized by the set of different angles between neighboring bonds when projected on a plane perpendicular to the screw axes. This definition establishes a new chemical relationship between equivalent aristotypes for a crystal polymorphism.

A very interesting aspect is the appearance of a glassy phase with low density (see Table I). The thermodynamical data of SiO_2 glass are similar to those of cristobalite, indicating an intrinsic relation between this crystalline and the glassy phase of SiO_2.[16] What role is played by the polymorphism in this context? Here, we should like to notice the following points:

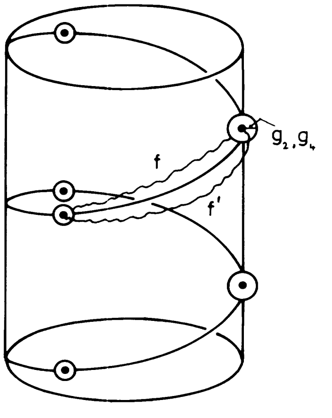

FIG. 4. Short-range forces in the cylinder model (for the definition of the various force constants, see text).

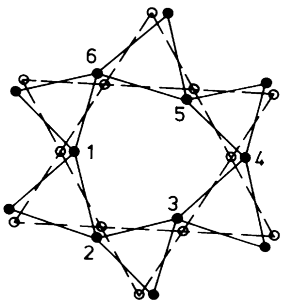

FIG. 5. $\beta \rightarrow \alpha$ transition in the cylinder model. The full lines connect the elements for the α-quartz structure, while the broken lines represent the β-quartz structure.

(i) The tetrahedral structures of SiO_2 correspond to the "bond stability" limit of a glassy structure[17] if the oxygen polarizability is taken into account.[18] (ii) The glass-forming process implies a sufficiently rapid cooling of liquid SiO_2 in order to avoid a lock-in to one of the crystalline phases. This means that dynamical structural fluctuations of all phases are present in the undercooled liquid. Consequently, solidification may begin by nucleation of microclusters with different spiralities yielding a eutecticlike mixture of frozen-in structural fluctuations.[19] A locally optimized "chaotic" solid is obtained where the cristobalite structure is dominating (because of its low density) but mixed up with small clusters of trydimite, quartz, etc.[20] This description is similar to the "topological defect" model of glasses.[21] (iii) In the case of ice it is known that a vitreous phase exists, too.[1] We suppose that this phase should exhibit structural features similar to those of silica glass.

In conclusion, we have shown that the polymorphism of SiO_2 and ice may be understood in terms of a nonlinear (ϕ^4) bond model for tetrahedrally coordinated insulators containing nonlinear bonds of O^{2-} or H, respectively. The symmetry principle of the polymorphism is demonstrated to be a ring of different commensurable spiralities, each one defining a "top" symmetrical structure (aristotype). The glassy phase appears as a highly incommensurate ("chaotic") phase of metastable nature.

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