
**STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY**

Towards Quantum Geophysics: Deductive Molecular Mechanics of High- and Low-Pressure Silica Polymorphs

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Received February 17, 2023; revised February 17, 2023; accepted March 2, 2023

Abstract—In the present paper we apply an analytical approach based on the (Quantum) deductive molecular mechanical (DMM) to the principal component of upper and middle Earth crust—silica (SiO₂) to study its polymorphs, trying to cover different coordination patterns occurring, respectively at ambient and somewhat higher pressures. Some characteristic structure features of either family of polymorphs are reproduced with a reasonable precision within a very simple physically sensible model. Specifically, the microscopic nature of the instability of the low-pressure phases towards Si–O–Si bending is revealed eventually paving a way towards understanding the entire field of “tetrahedral” polymorphs. As for higher-pressure “octahedral” polymorphs, some “proof-of-concept” estimates are performed, showing a perspective way of extending DMM technique towards higher pressures in a more numerical than analytical fashion.

DOI: 10.1134/S0036024423100242

1. INTRODUCTION

The first most widespread¹ mineral in the Earth crust is silica (SiO₂) [1]. It is characterized by a wide diversity of crystalline forms featuring different coordination types/numbers either for Si- or O-atoms. These forms show deep analogies with similar structures of group IV elements [2] and water [3]. Their variety is illustrated by Table 1 and Fig. 1.

As one can conclude from it, the entire range of densities corresponding to the specific volume V_{SiO_2} between 330 and 224 Bohr³/SiO₂ is occupied by the polymorphs with coordination numbers CN(Si) = 4, CN(O) = 2.² Somewhere between 225 and 170 Bohr³ the coordination numbers change to CN(Si) = 6, CN(O) = 3 in higher density (higher pressure) phases. Although the entire range of larger specific volumes of ~330–224 Bohr follows the same local coordination pattern—vertex sharing SiO₄ tetrahedra, the specific structures viewed from the crystallographic point of view are pretty different (see column “Symmetry” of Table 1).

If one considers these phases within a standard numerical approach of solid state quantum chemistry (PAW/DFT paradigm, see e.g., [13]), like in [14, 15],

each of chemically identical phases must be addressed separately since the space group, Brillouin zone, Bloch states, etc. are completely different [16].

As an alternative to the quantum chemical treatment of silica polymorphs, force field methods [17–19] targeted towards them have been developed [20–22]. They are based on two-center interactions, fundamentally Coulomb ones, of some effective atomic charges complemented by various repulsion and dispersion terms [21], which are further complemented by charge equilibration procedures as suggested in [23] and with Morse potentials designed to emulate the chemical (covalent) bonding. The pairwise interactions implemented in these fields miss the directionality characteristic for covalent bonding. Having reached certain success in describing coarse features of the silica polymorphs like *c/a* ratio in quartz or V_{SiO_2} etc, more subtle features are not covered by the purely two-center atom-atomic potentials. One can even say that with their use the correct results are obtained for a wrong reason. More involved three-center parameterizations eventually reproducing even that which is called “many-body effects” (eventually covering the angular dependencies of the bonding interactions) are derived by implicitly including information about quantum/chemical effects through fitting the values of the two- and three-center parameters against a selection of DFT calculations.

¹ Or second, if one takes a freedom to ascribe water to minerals.

² Lower density—lower pressure.

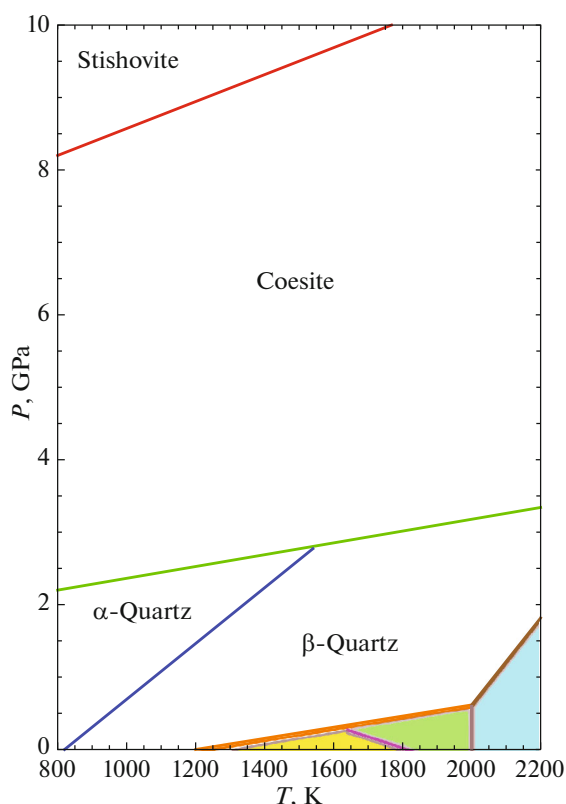


Fig. 1. P – T phase diagram of silica polymorphs [35, 36]. Strait boundaries between phases have following slopes: stishovite/coesite: 1.86×10^{-3} GPa/K; coesite/ α - β -quartz: 8.15×10^{-4} GPa/K; β -quartz/tridymite-cristobalite 7.69×10^{-4} GPa/K; α / β -quartz: 3.85×10^{-3} GPa/K; tridymite/cristobalite: -1.54×10^{-3} GPa/K (observe negative slope in the last case). “Minor” phases are color coded: tridymite – yellow; cristobalite—green; fluid—cyan.

Previously we developed a method of analysis of electronic and spatial structure of molecules and materials intermediate between standard quantum

chemistry and force field approaches—the Deductive Molecular Mechanics (DMM) [24–26]—which is free of the mentioned shortcomings and allows one to concentrate on the relevant physics. DMM is a model of electronic and spatial structure of molecules and crystals which permits to obtain the results of quantum chemical quality (effective charges, bond orders, interatomic separations and even heats of formation) with the computational costs of force field methods. The key feature of the DMM is the representation of the electronic structure of the material (or molecule) in terms of observable elements of electronic structure—generalized chromophores—like two-center bonds [27, 28] formalized within the theory of electronic group functions [29]. This produces the principal difference of the DMM from the traditional force fields [17–19]: the energy components in DMM are derived from well established quantum mechanical models of electronic structure. Thus, the DMM contains variables characterizing the electronic structure in addition to purely geometric ones of the usual force fields. Applied originally in the low-symmetry molecular context [25, 26, 30], later DMM has been extended to crystalline systems [16, 31–33]. In addition to significant reduction of computational costs it allowed us to develop analytical models for the structure-energy dependencies of the corresponding species, that could qualitatively (and even semi-quantitatively) reproduce phase diagrams of some fundamental elements (stoicheia) of ancients, namely, fire [34] (actually, of C_2 occurring in flames) and water [16] (of which we considered solid water phases—ices). Furthermore, we applied similar ideas to carbon allotropes [31–33] comparing diamond and graphite and being able to reproduce the energy difference of the order of 1 kJ/mol between them.

In the present paper, we propose an analogous consideration of the principal component of upper and middle Earth crust—silica. Two characteristic (limiting) cases of tridymite/cristobalite featuring the

Table 1. A selection of silica polymorphs addressed in the present paper

Polymorph	Symmetry	V_{SiO_2} (Bohr ³)	M	Si–O–Si, deg	Si ₂ O ₇ , deg
β -Cristobalite ¹	$Fd\bar{3}m$ [4]	355	4.45	180	60
β -Tridymite	$P6_3/mmc$ [5]	309	4.44	180	0/60 ²
α -Tridymite	$C222_1$ [5]	298		174/176	0/60 ²
α -Cristobalite	$P4_12_12$ [6]	289		146.5	60.83
β -Quartz	$P6_222$ [7]	266	4.40	153.3	
α -Quartz	$P3_121$ [8]	254		143.7	
Coesite	$C2/c$ [9, 10]	231		137.36/144.5/180	
Stishovite	$P4_2/mnm$ [11]	157	4.78/4.76 ³		

¹ In β -cristobalite Si atoms form the cubic diamond lattice and are bound by O bonds.

² Of three Si–O–Si bonds in the unit cell two are in eclipsed conformation and one in staggered.

³ Corresponds, respectively, to rutile I and rutile II structures [12].

tetrahedral coordination of the Si atoms by sp^3 oxygens and of seifertite/stishovite with the octahedral coordination of the Si atoms by sp^2 oxygen atoms are compared within the analytical approach.

The paper is organized as follows. In Section 2 we following [16] remind the general DMM scheme in relation to crystalline systems and specify the electronic groups (see below) relevant for description of the low- and high-pressure silica polymorphs. In Section 3 we provide results of our treatment and of some numerical experiments based on it. Details of the numerical modeling are given in Appendices. In Section 4 conclusions and outlook are given.

2. SILICA ENERGETICS WITHIN DMM

2.1. DMM Background

The formal definition of the deductive molecular mechanics (DMM) suitable for description of crystals is formed by the following ingredients: (i) the electronic wave function of the crystal is the (antisymmetrized) product:

$$\Psi_{\text{tot}}^{\text{el}} = \prod_{rg} \Psi_{rg}^{\text{el}}(N_g^{\text{el}}) \quad (1)$$

of the (group) functions $\Psi_{rg}^{\text{el}}(N_g^{\text{el}})$ [29] of coordinates of N_g^{el} electrons in each of the groups g in the unit cell r .

The functions Ψ_{rg}^{el} are formally defined by their expansion over the Slater determinants (denoted as usual by $|\dots\rangle$):

$$\Psi_{rg}^{\text{el}} = \sum_K C_K^{(g)} \left| h_{K_1}^{(rg)} \dots h_{K_{N_g^{\text{el}}}}^{(rg)} \right| \quad (2)$$

built upon the hybrid atomic orbitals $|h_k^{(rg)}\rangle$ (HOs) [24] ascribed to the g th group (spanning its carrier space) in the r th unit cell.

All the functions Eq. (2) are the same in all unit cells r in that sense that the expansion coefficients $A_{ka}^{(g)}$ of the HO $|h_k^{(rg)}\rangle$ over the AOs $|ar\rangle$ centered in the r th unit cell do not depend on r :

$$|h_k^{(rg)}\rangle = \sum_a A_{ka}^{(g)} |ar\rangle. \quad (3)$$

Under these assumptions the total electronic energy corresponding to the wave function Eqs. (1)–(3) acquires the form:

$$\begin{aligned} E_{\text{tot}}^{\text{el}} &= \sum_{rg} E_{rg}^{\text{el}} + \sum_{r', g' < rg} E_{rgr'g'}^{\text{int}} \\ &= \sum_g \left(E_{0g}^{\text{el}} + \sum_{rgg'} E_{0rgg'}^{\text{int}} \right), \end{aligned} \quad (4)$$

where the subscript rg refers to the g th group in the r th unit cell of the crystal and the quantities E_{rg}^{el} and $E_{rgr'g'}^{\text{int}}$ are, respectively, the mean values of the Hamiltonian operator for the group rg (eventually independent on r) and of the operator of interaction between groups rg and $r'g'$ (dependent only on the difference $(r - r')$). The second equality appears due to the fact that electronic groups are the same for the different unit cells and thus the sum of the energies of all electron groups $E_{rg}^{\text{el}} = E_{0g}^{\text{el}}$ in one unit cell and the sum of the energies of their (electrostatic) interactions $E_{rgr'g'}^{\text{int}} = E_{0g(r-r')g'}^{\text{int}}$ with all other groups in this and other unit cells. The variational principle then applies to the total energy Eq. (4) which is to be optimized with respect to geometry variables and the quantities $C_K^{(g)}$ and $A_{ka}^{(g)}$. This rounds up the formal description of the DMM scheme in the crystalline context.

2.2. Electronic Groups and Hybridizations in Silica Polymorphs

2.2.1. Low-pressure–low-coordination (“tetrahedral”) silica polymorphs.

(a) Geometry. The low-coordination low-pressure silica polymorphs all feature the SiO_4 tetrahedra sharing the O-vertices. The corresponding structure elements and their mutual arrangement are depicted in Fig. 2.

(b) Electronic groups: hybridizations and electron distribution. Electronic groups relevant for describing the structures of low-pressure “tetrahedral” polymorphs are the two-center two-electron polar-covalent Si–O bonds formed by the ideal sp^3 HOs of Si³ and sp^x HOs of O-atoms.

The description of the oxygen atom is more involved, but coincides with that of oxygen atom in water molecule [30]. Like there, oxygen atom bears two equivalent lone pairs (LP) and two equivalent HOs involved in bonding with Si atoms. Let s_σ^2 be the weight of the s -AO in the bonding HO (s_σ is respective *amplitude*—one of the coefficients $A_{ka}^{(g)}$ of Eq. (3)—other relevant amplitudes can be found in Appendix A1b Eq. (A.9)). Then the normalization condition $2s_\sigma^2 + 2s_{lp}^2 = 1$ immediately yields the s -weight in the oxygen LP's: $s_{lp}^2 = \frac{1}{2} - s_\sigma^2$. In terms of so defined s -weights/amplitudes the purely p -AOs characteristic for the LP's in the linear SiOSi units (e.g., in β -tridimite) refer to: $s_\sigma^2 = \frac{1}{2}$ ($s_\sigma = \frac{1}{\sqrt{2}}$ — sp -hybridiza-

³ The hybridization description of Si atoms is thus trivial.

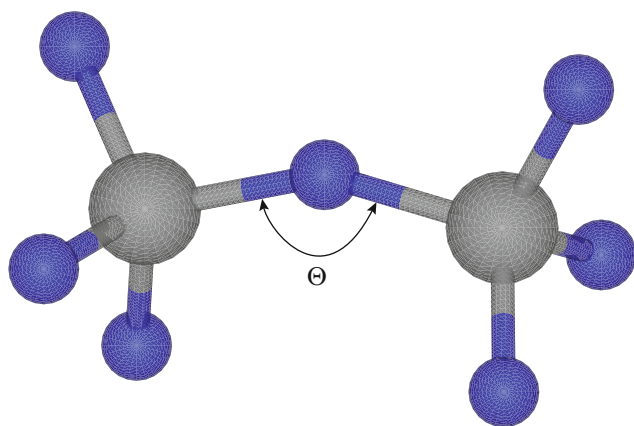


Fig. 2. Geometry of $\text{O}_3\text{Si}-\text{O}-\text{SiO}_3$ unit—two SiO_4 tetrahedra sharing a vertex. Color code: blue—oxygen, dark gray—silicon. For $\Theta = \pi$ the drawing shows the Si_2O_7 unit in the staggered conformation ($\text{O}-\text{Si}-(\text{O})-\text{Si}-\text{O}$ angle of 60°) like in β -cristobalite. The eclipsed conformation refers to the $\text{O}-\text{Si}-(\text{O})-\text{Si}-\text{O}$ angle of 0° . In β -tridymite half of the Si_2O_7 units are in the staggered and another half in the eclipsed conformation. They slightly differ by the Coulomb energy with a minor preference towards the staggered conformation. We introduce an angle $\vartheta = \frac{1}{2}(\pi - \Theta)$ describing the deformation of the $\text{Si}-\text{O}-\text{Si}$ angle to further work with “small” quantities. Picture is produced with use of the VESTA 3 software [37].

tion of the O atom). For the foreseen bending of the $\text{Si}-\text{O}-\text{Si}$ unit the sp -hybridization tends towards the sp^3 -one with $s_\sigma^2 = \frac{1}{4}\left(s_\sigma = \frac{1}{2}\right)$; this transition is trigonometrically parameterized as:

$$s_\sigma = \frac{\cos \zeta}{\sqrt{2}}, \quad (5)$$

where $\zeta = 0$ corresponds to the sp -hybridization. The lower s -weights in the bonding O-hybrids appear for $\zeta \neq 0$. According to [30], the angle between two bonding HOs reads

$$-\frac{\cos^2 \zeta}{2 - \cos^2 \zeta}$$

and one between the LP's:

$$-\frac{1 - \cos^2 \zeta}{1 + \cos^2 \zeta}.$$

Remarkably, the angle between bonding hybrids must not coincide with the angle between $\text{Si}-\text{O}$ bonds: $\Theta = \pi - 2\vartheta$ since they are controlled by two indepen-

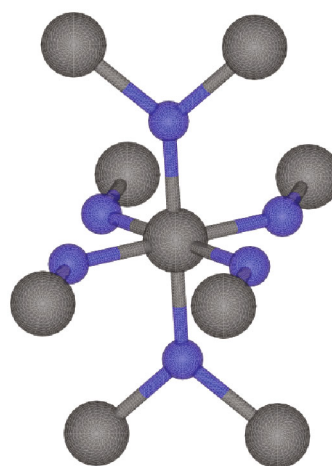


Fig. 3. Structure of the rutile-like polymorph of silica—stishovite. The overall view of the structure formed by SiO_6 octahedra each sharing two of its *equatorial* edges with two its neighbors; four *equatorial* O-atoms serve as *axial* ones in four other octahedra whereas the *axial* atoms serve as *equatorial* ones in *four* other octahedra and belong to their shared edges. Picture is produced with use of the VESTA 3 software [37].

dent variables ϑ and ζ . This is a characteristic feature of the DMM approach taking in the consideration chemical nature of the interactions.

Electron distribution within the $\text{Si}-\text{O}$ bonds in the silica polymorphs featuring SiO_4 unit derives from the simplistic two-electron two-orbital model of σ -bond. A single electronic structure variable Ψ suffice to construct the two-center MO—linear combination of the sp^3 -hybrid of Si atom with the coefficient $\sin \Psi$ and the O-hybrid ascribed to the $\text{Si}-\text{O}$ bond with the coefficient $\cos \Psi$. This yields the population of the *oxygen* σ -HO ascribed to the bond and the Coulson bond order (BO) between the Si and O HOs as:

$$\begin{aligned} P_\sigma &= \cos^2 \Psi, \\ B_\sigma &= \sin \Psi \cos \Psi. \end{aligned} \quad (6)$$

The atomic effective charges as well derive from the oxygen σ -HO population:⁴

$$4P_\sigma - 2 = -Q \text{ O},$$

$$4 - 8P_\sigma = 2Q \text{ Si}.$$

⁴ The count is as follows: core charge of oxygen equals to six; it is compensated by four electrons in two LPs which yields two. P_σ is the population of the bonding HO for each spin projection which, thus, must be multiplied by two for two spin projections and once again by two for two bonds.

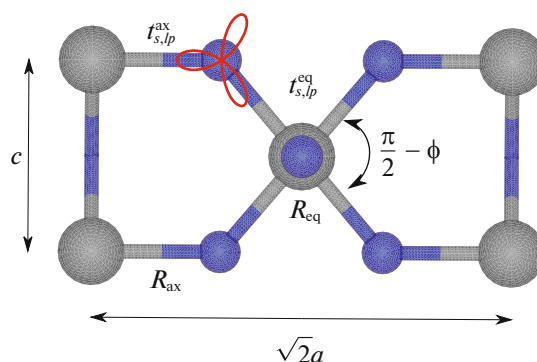


Fig. 4. The cut-off of the rutile structure showing one SiO_6 octahedron along the $a - b$ crystallographic direction, i.e., perpendicular to its *equatorial* plane. Geometry parameters are explained in the text. The red trifolium represents somewhat deformed sp^2 -hybrids. The lobe directed perpendicularly to the crystallographic c direction (along the Si–O bond which is *horizontal* in the picture) represents the axial oxygen lone pair interacting with the s -AO of the upper left Si atom. Remarkably, the direction of the slanted Si–O bond does not generally coincide with the direction of the corresponding HO (represented by the lobe pointing to the right and down).

2.2.2. High-pressure–high-coordination (“octahedral”) polymorphs.

(a) Geometry and hybridization. The spatial structure of a higher-pressure/density silica polymorph—stishovite [11] is the rutile structure formed by SiO_6 octahedra sharing edges and vertices (Fig. 3).

From the point of view of electronic structure stishovite describes as an assembly of coordination compounds of the nontransition element Si [38]. The octahedral coordination of Si atom featuring sp AO's assumes no hybridization [38]. In the idealized rutile structure (dubbed as rutile II in [12]) the octahedra are perfect and the angles between all Si–O bonds are equal to $\frac{\pi}{2}$. In the experimental rutile-like structures the octahedra are deformed so that the equatorial SiO_4 square (with the $2R_{\text{eq}}$ diagonal, Fig. 4) are deformed in a rectangle of the shape controlled by the angle ϕ . Two “axial” bonds are somewhat longer than four equatorial bonds $R_{\text{ax}} > R_{\text{eq}}$ so that we set $R_{\text{ax}} = R + 2r$; introducing the relevant geometry deformation variable r with $R = \frac{1}{3}(R_{\text{ax}} + 2R_{\text{eq}})$. In this case the ratio of the lattice parameters (under further assumption $R_{\text{ax}} = R_{\text{eq}} = R$) is:

$$\frac{a}{c} = \frac{1 + \sqrt{(1 + \sin \phi)/2}}{\sqrt{1 - \sin \phi}} = 1 + \frac{1}{\sqrt{2}} \approx 1.707 \quad (7)$$

with the latter numerical value characteristic for the ideal structure ($\phi = 0$).

Remarkably, the ideal (octahedral) geometry does not conform with the ideal sp^2 -hybridization of the oxygen atoms. Indeed, the ideal angles between Si–O bonds are $\frac{\pi}{2}$, whereas the angles between ideal sp^2 -hybrids are $\frac{2\pi}{3}$ (as schematically shown in Fig. 4). In order to align the equatorial bonds with the ideal hybrids the equatorial square needs to be squeezed so that the angle ϕ becomes $-\frac{\pi}{6}$. This yields the ratio of

crystallographic parameters $a/c = \sqrt{\frac{3}{2}} \approx 1.225$ for the rutile I structure [12]. The parameters of all observed rutile structures lie between this value and the above limit Eq. (7), as stated in [12].⁵

(b) Electronic groups. In the real (rutile/stishovite) structure O-atoms form one (longer) axial and two (shorter) equivalent equatorial Si–O bonds. Thus the involved hybrids are deformed sp^2 -hybrids (the fourth oxygen hybrid is a pure p -AO pointing normally to the plane of three Si–O bonds). Since two equatorial hybrids are equivalent, the weights of the s -AO in these hybrids satisfy the condition;⁶

$$2s_{\text{eq}}^2 + s_{\text{ax}}^2 = 1,$$

and one variable (ζ), as previously, suffice to describe the hybridization of such an atom. The

⁵ In stishovite this ratio is accordingly somehow intermediate: $a/c = 1.567$.

⁶ In the ideal sp^2 -HOs these weights are equal to $\frac{1}{3}$.

explicit forms are quite cumbersome and are moved in the Appendix A.1.b.

(c) Electron distribution. The set of 10 orbitals: four sp -AOs of Si and six oxygen hybrids span an

electronic group called the close ligand shell (CLS) as suggested in [39]. They are populated by twelve electrons. In an ideal octahedron, the 10×10 Fock operator for the CLS has the form:

$$\begin{pmatrix} \alpha_s & 0 & 0 & 0 & \beta_{s,lp} & \beta_{s,lp} & \beta_{s,lp} & \beta_{s,lp} & \beta_{s,lp} & \beta_{s,lp} \\ 0 & \alpha_p & 0 & 0 & \beta_{p,lp} & -\beta_{p,lp} & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha_p & 0 & 0 & 0 & \beta_{p,lp} & -\beta_{p,lp} & 0 & 0 \\ 0 & 0 & 0 & \alpha_p & 0 & 0 & 0 & 0 & \beta_{p,lp} & -\beta_{p,lp} \\ \beta_{s,lp} & \beta_{p,lp} & 0 & 0 & \alpha_{lp} & 0 & 0 & 0 & 0 & 0 \\ \beta_{s,lp} & -\beta_{p,lp} & 0 & 0 & 0 & \alpha_{lp} & 0 & 0 & 0 & 0 \\ \beta_{s,lp} & 0 & \beta_{p,lp} & 0 & 0 & 0 & \alpha_{lp} & 0 & 0 & 0 \\ \beta_{s,lp} & 0 & -\beta_{p,lp} & 0 & 0 & 0 & 0 & \alpha_{lp} & 0 & 0 \\ \beta_{s,lp} & 0 & 0 & \beta_{p,lp} & 0 & 0 & 0 & 0 & \alpha_{lp} & 0 \\ \beta_{s,lp} & 0 & 0 & -\beta_{p,lp} & 0 & 0 & 0 & 0 & 0 & \alpha_{lp} \end{pmatrix} \quad (8)$$

in the original AO/HO basis, with the quantities α_s , α_p , α_{lp} , $\beta_{s,lp}$, $\beta_{p,lp}$ given in the Appendix B.

Symmetry analysis yields very simple picture based on classification of one-electron states according to the irreducible representations of the octahedron symmetry group O_h . Specifically, Si s -AO is a_1 , Si p -AO's is t_{1u} . The combinations of the idealized oxygen sp^2 -HOs form a reducible representation of O_h which splits in the direct sum: $a_1 \oplus t_{1u} \oplus e_g$ of the irreducible representations. Explicit forms of the symmetry adapted combinations of HO's are:

$$\begin{aligned} |a_1\rangle &= \frac{1}{\sqrt{6}}(\chi_x + \chi_{-x} + \chi_y + \chi_{-y} + \chi_z + \chi_{-z}), \\ |t_{1u\gamma}\rangle &= \frac{1}{\sqrt{2}}(\chi_\gamma - \chi_{-\gamma}), \end{aligned} \quad (9)$$

$$|e_{gc}\rangle = \frac{1}{\sqrt{12}}(-\chi_x - \chi_{-x} - \chi_y - \chi_{-y} + 2\chi_z + 2\chi_{-z}).$$

Here χ_γ stands for the oxygen sp^2 -HO centered on the O atom shifted to the direction γ ($=x, y, z$) relative to the central Si atom. They are depicted in Fig. 5.

In the symmetry adapted basis Eq. (9) the Fockian splits in four 2×2 blocks of which three are identical acting in the t_{1u} subspace, one 2×2 block referring to the a_1 subspace, and two identical diagonal elements (1×1 blocks) belonging to the e_g symmetry. The electronic structure variables of the CLS (symmetrized SiO6 octahedron) are thus the angles Φ and Ψ providing amplitudes of the Si s - and p -AO's in the occupied (bonding) MO's of the a_1 and t_{1u} symmetries (denoted by the “-” superscript referring to the sign at the

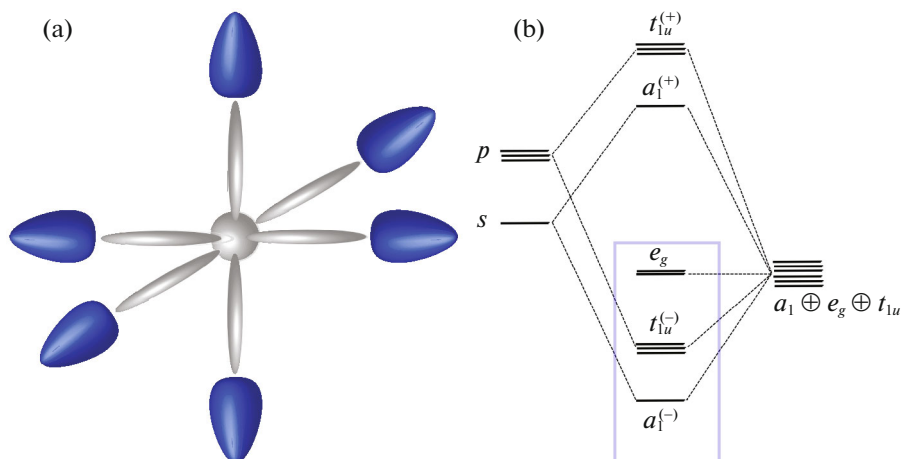


Fig. 5. (a) Scheme of the atomic and hybrid orbitals pertaining to the close ligand sphere (CLS) of the Si atom in the idealized octahedral structure. (b) Molecular orbital diagram of the idealized CLS; the occupied MOs are encircled by a blue rectangle.

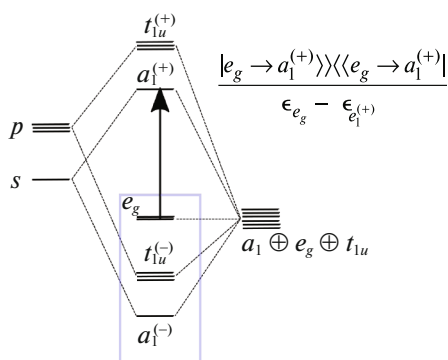


Fig. 6. Orbital scheme of deformation of the electronic structure of idealized Si CLS upon its transition to the realistic one.

square root in the expressions for the orbital energies of the occupied MOs):

$$\begin{aligned} |a_1^{(-)}\rangle &= \sin \Phi |s\rangle + \cos \Phi |a_1\rangle, \\ |t_{1u\gamma}^{(-)}\rangle &= \sin \Psi |p_\gamma\rangle + \cos \Psi |t_{1u\gamma}\rangle, \end{aligned} \quad (10)$$

$|s\rangle$ and $|p_\gamma\rangle$ refer to the respective Si-AO's. The components of the one-electron density matrix are:

$$\begin{aligned} B_s &= \frac{1}{\sqrt{6}} \sin \Phi \cos \Phi, \\ B_p &= \frac{1}{\sqrt{2}} \sin \Psi \cos \Psi. \end{aligned} \quad (11)$$

The coulson bond orders between the s -, p -AO's of the Si atom with an sp^2 -HO of oxygen. The electronic population of the respective AOs/HOs (for each of the two spin projections) are:

$$\begin{aligned} P_s &= \sin^2 \Phi, \\ P_p &= \sin^2 \Psi, \\ P_{lp} &= \frac{1}{3} + \frac{\cos^2 \Phi}{6} + \frac{1}{2} \cos^2 \Psi, \end{aligned} \quad (12)$$

producing the density matrix of CLS:

$$\begin{pmatrix} P_s & 0 & 0 & 0 & B_s & B_s & B_s & B_s & B_s & B_s \\ 0 & P_p & 0 & 0 & B_p & -B_p & 0 & 0 & 0 & 0 \\ 0 & 0 & P_p & 0 & 0 & 0 & B_p & -B_p & 0 & 0 \\ 0 & 0 & 0 & P_p & 0 & 0 & 0 & 0 & B_p & -B_p \\ B_s & B_p & 0 & 0 & P_{lp} & 0 & 0 & 0 & 0 & 0 \\ B_s & -B_p & 0 & 0 & 0 & P_{lp} & 0 & 0 & 0 & 0 \\ B_s & 0 & B_p & 0 & 0 & 0 & P_{lp} & 0 & 0 & 0 \\ B_s & 0 & -B_p & 0 & 0 & 0 & 0 & P_{lp} & 0 & 0 \\ B_s & 0 & 0 & B_p & 0 & 0 & 0 & 0 & P_{lp} & 0 \\ B_s & 0 & 0 & -B_p & 0 & 0 & 0 & 0 & 0 & P_{lp} \end{pmatrix}.$$

The total population of the Si atom is:⁷

$$2P_s + 6P_p,$$

and its effective charge ($2Q$) reads

$$4 - 2P_s - 6P_p.$$

We see that the solution of the electronic problem for the idealized CLS of the Si atom is pretty simple. However, this is not enough. In the true stishovite structure, the octahedra are inherently deformed, as it has been mentioned above, and will be explained in more details below. In the deformed octahedra the electronic structure is as well deformed. The electronic structure of real CLS derives from the symmetrized model by adding perturbation to the Fockian Eq. (8). Within the DMM theory of coordination compounds of nontransition elements [38, 39], it can be shown that the structure transformation of the ideal octahedron to the deformed one characteristic for experimental stishovite structure induces a perturbation of the electronic structure which is equivalent to a partial depopulation of the highest occupied molecular orbital (HOMO of the ideal octahedron) of the e_{gc} symmetry and corresponding population of its lowest unoccupied molecular orbital (LUMO) of a_1 symmetry (Fig. 6). It can be represented as a replacement of the HOMO of the e_{gc} symmetry by its linear combination with the LUMO of a_1 symmetry. This move is allowed, since the deformed octahedron does not possess the symmetry of the ideal one. Thus, we write:

$$\begin{aligned} |e_{gc}\rangle &\rightarrow \cos \varphi |e_{gc}\rangle + \sin \varphi |a_1^{(+)}\rangle, \\ |a_1^{(+)}\rangle &= \cos \varphi |s\rangle - \sin \varphi |a_1\rangle, \end{aligned} \quad (13)$$

where a variable φ is introduced in addition to the above set of electronic structure variables Φ, Ψ, ζ . The corresponding energy contribution to the energy of the deformed SiO_6 octahedron reads:

$$\sin^2 \varphi (\epsilon_{a_1^{(+)}} - \epsilon_{e_g}) + \sin 2\varphi \langle e_{gc} | V | a_1^{(+)} \rangle, \quad (14)$$

where $\epsilon_{a_1^{(+)}}$, ϵ_{e_g} are the orbital energies (eigenvalues of the Fockian Eq. (8)) of the ideal “octahedral” model and $\langle e_{gc} | V | a_1^{(+)} \rangle$ is the matrix element of the operator which upon adding it to Eq. (8) produces the Fockian of the distorted CLS. The minimum of Eq. (14)—the only φ -dependent contribution to the total energy of stishovite—with respect to φ in the lowest order coincides with the familiar 2nd order perturbative estimate:

$$-\frac{\langle e_{gc} | V | a_1^{(+)} \rangle^2}{\epsilon_{a_1^{(+)}} - \epsilon_{e_g}}.$$

⁷ Coefficients take care about two spin projections.

Table 2. Intraatomic Coulomb repulsion energies for Si and O atoms in the tetrahedral and octahedral polymorphs. Coefficients “2” in the “O”-column take care about two O-atoms in each formula unit

E	Si	O
Tetra	$28G^{\text{Si}}[1 - P_{\sigma}]^2$	$2G^{\text{O}}[6(1 + P_{\sigma}^2) + 16P_{\sigma}]$
Octa	$G^{\text{Si}}[P_s^2 + 15P_p^2 + 12P_sP_p]$	$2G^{\text{O}}[1 + 12P_p + 15P_p^2]$

The latter, however, cannot be employed for optimization with respect to the system variables since the denominator is driven to zero throughout this process. For that reason we below consider ϕ on the equal footing with other variables. This lifts the condition usually imposed upon the perturbation, to be small. In the proposed variational scheme it may be arbitrary.

2.3. Energy Components

With the above descriptions of the electronic structures of “tetrahedral” and “octahedral” SiO_2 polymorphs given in terms of the group functions, the hybridizations of involved orbitals and elements of density derived from them, we see that the repertory of the electronic structure variables required for describing either of polymorphs is rather limited. Specifically, these are two electronic structure variables Ψ, ζ for “tetrahedral” polymorphs and somewhat more abundant Ψ, Φ, ζ, ϕ set for “octahedral” ones. In either case they are to be complemented by the relevant geometry variables: R, ϑ (for “tetrahedral”) and R, r, ϕ (for “octahedral”). According to the general variational principle [27, 40] inherited by the DMM setting, the equilibrium values of either electronic or geometry variables need to be determined from the energy minimum condition. Like in force fields, the energy in DMM is given through its components, but in variance with the former the required components are derived from quantum mechanical models. Usually such models (particularly those which are used for numerical modeling [13] are pretty sophisticated), thus, we accept a simpler setting, keeping the most physically important contributions: attractions of valence electrons to atomic cores (nuclei screened by deep electronic shells), Coulomb interactions between the valence electrons, and the most important *quantum* contribution: the resonance or electron hopping—the energy contribution appearing due to transitions of electrons between the HOs centered at different atoms—the one ultimately responsible for the band formation in the tight-binding approximation [41–44] of solid state physics. The Coulomb interactions are treated “on average”—the same values are used irrespective to the differences between *s*- and *p*-AOs of the same atom. By contrast, the attractions of electrons in an HO to the core, at which it is centered and the res-

onance are strongly dependent on the ratio of *s*- and *p*-AOs in the HO. In case of resonance interactions the hybridization dependence is accompanied by geometry one. This corresponds to the CNDO⁸ setting of semi-empirical quantum chemistry [45], which covers the most important physics.

2.3.1. One-center terms. The systems considered in the present paper are formed by *atoms* featuring *s*- and *p*-AOs only (hereinafter referred to as *sp*-elements). For them the one-center quantities can be easily written down.

(a) Core attractions. For HO’s of *sp*-elements the core attraction matrix elements depend on the weights of the *s*-AOs in *m*th HO: s_m^2 ($E = \text{Si, O}$) [24]:

$$U_m^E = U_{pp}^E + (U_{ss}^E - U_{pp}^E)s_m^2, \quad (15)$$

where U_{ss}^E, U_{pp}^E are the core attraction parameters for *s*- and *p*-AOs of the atoms of chemical elements *E* (see Appendix A). The specific dependencies of the involved weights on the variable ζ controlling the hybridization and consequent specific expressions for the core attractions are assembled in Appendix A.1.b.

(b) One-center repulsions. Simple analysis shows that in a four-orbital atom the expression for one-center Coulomb repulsion of electrons comes from four intra-orbital interactions each proportional to squared density elements on each orbital combined with six inter-orbital interactions each proportional to quadruple products of the density elements in involved orbitals. This yields overall 28 individual contributions each scaling as the parameter of electron–electron repulsion characteristic for the given atom: G^E , $E = \text{Si, O}$. With this we derive the intraatomic Coulomb repulsion contributions assembled in Table 2.

2.3.2. Two-center terms. (a) Effective charges and cores. The predominant two-center terms in DMM arise from the Coulomb interactions between charged particles—nuclei and electrons—of the system. The actual form of these interactions in the models employing AOs may be different (for [27]). At the CNDO level [45] one distinguishes the Coulomb repulsion of the atomic cores $\propto R^{-1}$, that of the attraction of (valence) electronic clouds to an alien core $\propto V(R)$, and the repulsion between the clouds centered at different atoms $\propto \gamma(R)$ —two latter having finite limits at the vanishing interatomic separation R . Setting $V(R)$ approximately equal to $\gamma(R)$ reduces the interaction of atomic charge distributions into that of the effective charges Q_i of atoms *i* (core charges Z_i minus total electronic population P_i of the valence orbitals)

⁸ Complete neglect of differential overlap.

proportional to $\gamma(R)$ and the repulsion of the cores with a “Yukawa”-like potential $Y(R)$:

$$Q_1 Q_2 \gamma(R) + Z_1 Z_2 Y(R); \quad Y(R) = R^{-1} - \gamma(R). \quad (16)$$

“Yukawa” potential diverges as $R \rightarrow 0$ preventing the collapse of the system, but decays exponentially with increasing interatomic separation, which justifies the name. Thus it is enough to take the “Yukawa” terms into account only for the nearest neighbors: (i) four O-atoms bound with a Si atom and (ii) among these four O-atoms themselves—six interactions, exactly like in the ice model [16]. Similarly, the cloud repulsion $\gamma(R)$ is taken into account for the same set of atoms otherwise the two-center terms beyond the nearest neighbors reduce to the interactions of the effective charges Q_i which already can be approximated by the usual Coulomb R^{-1} potential. The explicit expressions are somewhat tedious, thus we move them in the Appendix A.1.a.

(b) Resonance contribution in Si–O bonds. The resonance contribution is most complicated since it involves rather sophisticated dependence on hybridization of the O-atom and the geometry parameters. This is the only directionally dependent energy contribution affecting the local geometry. The resonance contributions have simplest form in the basis of HOs [24]. Specifically, in the “tetrahedral” polymorphs it reads:

$$-16B_\sigma t_\sigma,$$

where B_σ is given by Eq. (6) and t_σ is the interhybrid resonance matrix element. Somewhat more involved expression applies in the “octahedral” case:

$$-24(B_s t_{s,lp} + B_p t_{p,lp}),$$

which corresponds to six Si–O interactions with the bond orders B_s, B_p given by Eq. (11), $t_{s,lp}, t_{p,lp}$ resonance matrix elements between s - and p -AOs of Si atom and the oxygen HOs, describing electron hopping from Si to O and from O to Si, taken twice for two spin projections.

The sophisticated geometry/hybridization dependence of the quantities $t_\sigma, t_{s,lp}, t_{p,lp}$ originates from the general expression for the resonance matrix element between HOs [24]:

$$\begin{aligned} t_m &= t_{\sigma\sigma}^{\text{SiO}} s_m^{\text{Si}} s_m^{\text{O}} + t_{\sigma\zeta}^{\text{SiO}} s_m^{\text{Si}} (\vec{v}_m^{\text{O}}, \vec{e}_{\text{SiO}}) \\ &+ t_{\zeta\sigma}^{\text{SiO}} (\vec{v}_m^{\text{Si}}, \vec{e}_{\text{SiO}}) s_m^{\text{O}} + t_{\pi\pi}^{\text{SiO}} (\vec{v}_m^{\text{Si}}, \vec{v}_m^{\text{O}}) \\ &+ (t_{\zeta\zeta}^{\text{SiO}} - t_{\pi\pi}^{\text{SiO}}) (\vec{v}_m^{\text{Si}}, \vec{e}_{\text{SiO}}) (\vec{v}_m^{\text{O}}, \vec{e}_{\text{SiO}}). \end{aligned} \quad (17)$$

Here, $\vec{e}_{\text{SiO}}$ is the unity-length vector pointing from Si to O; s_m^{E} , $\text{E} = \text{Si}, \text{O}$ are the amplitudes of s -AOs of the respective atoms in the hybrids ascribed to the m th

bond, $\vec{v}_m^{\text{E}}$ are the triples of amplitudes of the p -AOs ($\gamma = x, y, z$) in the expansion of the HOs. Under 3D rotations these triples transform as 3-vectors which explains the accepted notation for this specific type of

the general expansion coefficients $A_{ka}^{(g)}$, Eq. (3). The quantities $t_{\mu\nu}^{\text{SiO}} = t_{\mu\nu}^{\text{SiO}}(R)$; $\mu, \nu = \sigma, \zeta, \pi$ are known functions of the interatomic Si–O separations, which represent respectively, the resonance matrix elements between the AO’s centered on the Si and O atoms with subscripts σ, ζ referring, respectively, to the s - and p -AOs directed along the $\vec{e}_{\text{SiO}}$ vector (taking, thus, the part of the z -axis of so called diatomic coordinate frame), and π refers to p -AOs orthogonal to it (notation refers to the π -symmetry with respect to the local z -axis $\vec{e}_{\text{SiO}}$).

Due to considerable sophistication of the relevant expressions they are moved to Appendix A.1.c. Here we provide only the final results. Specifically, for the Si–O bond in a “tetrahedral” silica polymorph we arrive to not that much involved expression:⁹

$$\begin{aligned} t_\sigma &= \frac{1}{2\sqrt{2}} \left[\cos \zeta (\sqrt{3} t_{\zeta\sigma}(R) + t_{\sigma\sigma}(R)) \right. \\ &\left. - (\sqrt{3} t_{\zeta\zeta}(R) + t_{\sigma\zeta}(R)) (\sin \vartheta \sin \zeta + \cos \vartheta) \right]. \end{aligned} \quad (18)$$

For the “octahedral” case the explicit formulae for $t_{s,lp}, t_{p,lp}$ derive from the same general expression Eq. (17) supplied by the relevant values for the HOs’ amplitudes $(s_m^{\text{E}}, \vec{v}_m^{\text{E}})$ and interatomic vectors $\vec{e}_{\text{SiO}}$. They are rather cumbersome, so we move them to Appendix A.1.c. Here we notice the following: as it is mentioned above, the solution for the electronic structure problem for the CLS of the Si atom, surrounded by six oxygens, derives from the symmetrized Fockian, in which all core-attraction matrix elements for oxygen LPs are the same and the axial and equatorial Si–O resonance matrix elements are the same. The latter is, however, formally incompatible with the square planar arrangement of the equatorial oxygen atoms. We, nevertheless, employ the resonance matrix elements between the ideal sp^2 O HOs and Si AOs:

$$\begin{aligned} 1t_{s,lp}^{\text{ax}}(R) &= \frac{1}{\sqrt{3}} (t_{\sigma\sigma}(R) - \sqrt{2} t_{\sigma\zeta}(R)), \\ t_{p,lp}^{\text{ax}}(R) &= \frac{1}{\sqrt{3}} (t_{\zeta\sigma}(R) - \sqrt{2} t_{\zeta\zeta}(R)) \end{aligned} \quad (19)$$

for constructing the symmetrized model and consider the difference between the matrix elements of the

⁹ We omit the superscripts referring to atoms, bearing in mind that the first Greek subscript refers to an AO of Si and the second to an AO of the O atom.

symmetrized model and exact ones as a part of the perturbation Eq. (14). The corresponding quite tedious explicit formulae are given in Appendix A.1.c.

(c) Effective exchange. There is a minor (as compared to the resonance) quantum mechanical contribution to the energy. We do not elaborate on its detailed nature here; more detailed description of its role in the DMM context can be found in [16]. It is proportional to the squared bond orders Eqs. (6), (11) and to the Coulomb interaction between the electronic clouds of two atoms. Specifically:

$$-8B_{\sigma}^2\gamma_{\text{SiO}}(R),$$

$$-12(B_s^2 + B_p^2)\gamma_{\text{SiO}}(R)$$

for “tetrahedral” and “octahedral” polymorphs, respectively.

2.3.3. Contributions dependent on global structure.

In the standard approach of solid state quantum chemistry even slightest variations of crystal symmetry require a separate consideration, since the space group, Brillouin zone, Bloch states etc completely differ. This is so despite the fact that different polymorphs may be chemically very close—definitely the case for the “tetrahedral” polymorphs of silica. For that reason, chemical similarity in standard approach is recovered *post factum*; e.g., using LOBSTER [46–48] or other tools used for projection of the PAW/DFT solutions upon some local atomic states recovering chemical individuality. Our approach is, by contrast from very beginning based on the local (HO) representation of the electronic structure stressing the chemical nature of the considered materials. Within it the polymorphs with similar local structure are basically equivalent. The variations of, say, overall symmetry, in their turn, fairly logically affect only the long-range energy contributions.

The only long-range contribution is the Coulomb interaction of the effective charges beyond the nearest neighbor SiO_4 and SiO_6 clusters as described in Section 2.2.3. Looking at the Coulomb terms, we notice that in a first approximation the interactions of the effective charges in a crystal reduce to the Madelung energy:

$$-\frac{MQ^2}{R},$$

where M is the Madelung constant characteristic for each crystalline structure (see e.g., [49]). This form of the interaction leads to a strong attractive contribution diverging at $R \rightarrow 0$. This is cured by the interactions between nearest neighbors Eqs. (A.1)–(A.4) Appendix A.1.a which provides (i) the *divergent repulsive* “Yukawa” terms acting between atomic cores and (ii) the interactions of the effective charges tending to a finite value (some combination of intraatomic Coulomb interactions of electrons) at $R \rightarrow 0$. Obviously,

the Coulomb energy of the effective charges located on the nearest neighbors:

$$-\frac{M_{\text{NN}}Q^2}{R}$$

must be subtracted from the Madelung energy. These contributions are:¹⁰

$$M_{\text{NN}} = \begin{cases} 8 - 3\sqrt{\frac{3}{2}} \approx 4.326 & \text{tetrahedron} \\ 12 - \frac{11}{\sqrt{2}} \approx 4.2218 & \text{octahedron} \end{cases}$$

so that the long-range remains of the Madelung energy are:

$$-\frac{\mu Q^2}{R} \quad (20)$$

with $\mu = M - M_{\text{NN}}$.¹¹ Obviously, μ are some relatively small structure dependent numbers.

Although the Madelung energies can be numerically calculated for whatever crystal structures, this does not completely solve our problem, since we need some analytical estimates of their variation upon small geometry changes. We, thus, notice that, say, bending of the Si–O–Si bond (see Fig. 2) from the point of view of other distant charges in the crystal is equivalent to appearance of effective dipole moments of the magnitude $QR \sin \vartheta$ at the original positions of the shifted oxygen atoms [16]. The energy of their interactions is proportional to their squares and inverse proportional to the cubes of separations between dipoles. All distances between dipoles can be expressed through the characteristic length scale: the Si–O separation R (like it is done for the Madelung energies), so that the dipole–dipole energy acquires the form

$$-\frac{\kappa Q^2 R^2 \sin^2 \vartheta}{R^3} = -\frac{\kappa Q^2}{R} \sin^2 \vartheta,$$

with some structure-dependent constant κ —ultimately an analog of the Madelung constants for the respective distribution of dipoles over crystal lattices. Combining the long-range terms together yields:

$$-\frac{Q^2}{R}(\mu + \kappa \sin^2 \vartheta), \quad (21)$$

which is employed in further analysis.

¹⁰In the case of octahedron the edge sharing is accounted.

¹¹For rutile I of [12] $M = 4.760$ so that $\mu = 0.538$; for rutile II of [12] $\mu = 0.561$; for cristobalite $M = 4.453$; $\mu = 0.127$, in tridimite $M = 4.44$, $\mu = 0.114$; in β -quartz $\mu = 0.077$.

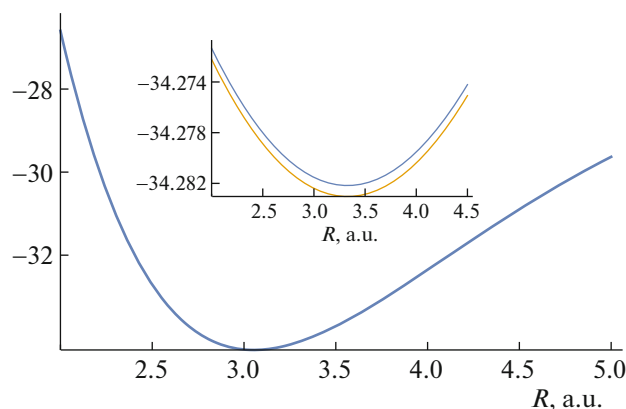


Fig. 7. Energy profile for tridimite (blue) and cristobalite (orange). The cristobalite energy profile lies lower due to a larger value of μ in its case. The minimum corresponds to interatomic separation of $R_0 = 3.05$ a.u.

3. RESULTS AND DISCUSSION

3.1. Analytical Theory of Tetrahedral Silica Polymorphs

3.1.1. Low-density/low-pressure polymorphs. Collecting all the terms described in previous Sections and Appendices yields the energy of a “tetrahedral” SiO_2 -polymorph in terms of two geometry variables (R and ϑ) and two electronic-structure variables (Ψ and ζ). Despite its rather involved form:

$$\begin{aligned}
 E_{\text{tot}} = & -2(1 - P_{\sigma})(3U_{pp}^{\text{Si}} + U_{ss}^{\text{Si}}) + 28G^{\text{Si}}(1 - P_{\sigma})^2 \\
 & + 2G^{\text{O}}(6(1 + P_{\sigma}^2)J_{\sigma}) - 8U_{pp}^{\text{O}}(1 - P_{\sigma}) \\
 & - 4(U_{ss}^{\text{O}} - U_{pp}^{\text{O}})(P_{\sigma} \cos^2 \zeta + \sin^2 \zeta) - 16B_{\sigma}t_{\sigma}(R) \\
 & - 8B_{\sigma}^2\gamma_{\text{SiO}}(R) - 8Q^2\gamma_{\text{SiO}}(R) + 6Q^2\gamma_{\text{OO}}\left(\sqrt{\frac{8}{3}}R\right) \\
 & + 96Y_{\text{SiO}}(R) + 216Y_{\text{OO}}\left(\sqrt{\frac{8}{3}}R\right) \\
 & - \frac{Q^2(\mu + \kappa \sin^2 \vartheta)}{R} + \Pi\Omega R^3 \cos^3 \vartheta,
 \end{aligned} \quad (22)$$

inspecting this and recollecting the expression Eq. (18) for $t_{\sigma}(R)$ and the definitions of the density components P_{σ}, B_{σ} Eq. (6) allows us to establish the symmetry relation which the energy function Eq. (22) satisfies:

$$E_{\text{tot}}(\Psi, R, \zeta, \vartheta) = E_{\text{tot}}(\Psi, R, -\zeta, -\vartheta). \quad (23)$$

Following a simple theorem [16] the above symmetry assures that (a):

$$\left. \frac{\partial E_{\text{tot}}}{\partial \zeta} \right|_{\zeta, \vartheta=0} = \left. \frac{\partial E_{\text{tot}}}{\partial \vartheta} \right|_{\zeta, \vartheta=0} = 0$$

and (b) if under the condition $\zeta = \vartheta = 0$, there is an extremum with respect to two *noninvertible* variables R

and Ψ it will be also an extremum with respect to all variables $\Psi, R, \zeta, \vartheta$.

The latter hypothesis can be easily checked. Indeed, upon substitution $\zeta, \vartheta = 0$ characteristic for tridimite/cristobalite polymorphs in Eq. (22), it reduces to

$$\begin{aligned}
 & 28G^{\text{Si}}(1 - P_{\sigma})^2 + 2G^{\text{O}}(6(P_{\sigma}^2 + 1)J_{\sigma}) \\
 & - 2(1 - P_{\sigma})(3U_{pp}^{\text{Si}} + U_{ss}^{\text{Si}}) - 4(U_{ss}^{\text{O}} + U_{pp}^{\text{O}})(1 + P_{\sigma}) \\
 & - \frac{8B_{\sigma}}{\sqrt{2}}[(\sqrt{3}t_{\zeta\sigma}(R) + t_{\sigma\sigma}(R)) - (\sqrt{3}t_{\zeta\zeta}(R) + t_{\sigma\zeta}(R))] \\
 & - 8B_{\sigma}^2\gamma_{\text{SiO}}(R) + Q^2[6\gamma_{\text{OO}}(\sqrt{83}R) - 8\gamma_{\text{SiO}}(R)] \\
 & + 96Y_{\text{SiO}}(R) + 216Y_{\text{OO}}(\sqrt{83}R) + \Pi\Omega R^3 - \frac{\mu Q^2}{R},
 \end{aligned} \quad (24)$$

where two upper rows contain the terms explicitly independent on the Si–O separation R , the 3rd row represents some contributions slowly varying with R , two further ones assemble the strongly R -dependent (“tectonic”) terms, and the bottom row assembles the terms dependent on global structure variables. Looking, first, at the 4th row we notice that the interaction of the nearest neighbors’ effective charges ($\propto Q^2$) is always attractive (has positive derivative with respect to R) and flows to a finite (negative) value at $R \rightarrow 0$ together with its derivative which in the same limit is as well finite and positive. The derivative of this interaction with respect to R remains positive, but flows to zero in the opposite limit ($R \rightarrow \infty$) like $\propto R^{-2}$. The same applies to the effective exchange ($\propto B_{\sigma}^2$) term. On the other hand, the repulsive core-core terms in the 5th row are positive and divergent with the divergent negative derivative with respect to R at $R \rightarrow 0$. They remain negative, but decay exponentially with $R \rightarrow \infty$. The remnant attractive divergency $\propto R^{-1}$ at $R \rightarrow 0$ of the Madelung ($\propto \mu$) energy is fully compensated by the repulsive divergency $\propto R^{-1}$ of the “Yukawa” terms (compare the $Z_{\text{Si}}Z_{\text{O}}$ and Z_{O}^2 multipliers in Eqs. (A.3), (A.5) with the highest possible estimate of $Q^2 = 4$ and values of μ mentioned above). Assembling these observations together, we see that the derivative of the sum of 5th and 6th rows is negative in the vicinity of $R \gtrsim 0$ and turns positive for $R \rightarrow \infty$.¹² This constitutes the conditions of the Bolzano theorem in its original formulation [50, 51]. Namely, the derivative of the sum of 5th and 6th rows has different signs at small and large values of R (respectively, <0 and >0), so that there exists a point

¹²Beyond the range of the exponential decay of the “Yukawa” terms, they are superseded by positive derivative of the interaction of effective charges.

R_0 where the derivative of the sum of 5th and 6th rows vanishes and thus provides an extremum to the “tectonic” terms. The R -independent terms of the 1st and 2nd rows do not change either condition or the conclusion of the theorem.^{13,14} We also easily conclude that the extremum at R_0 is a minimum with respect to R .¹⁵ These theoretical conclusions are confirmed by direct illustrative calculation (performed with use of parameterization described in Appendix A.2) whose results are depicted in Fig. 7. The obtained geometry of the linear Si_2O_7 units ($\vartheta = 0$) corresponds to the high-temperature forms of the low-density/pressure cristobalite and tridimite polymorphs [4, 5, 52–57].

3.1.2 (In)stability of tetrahedral polymorphs. The nature of the energy extremum found above can be revealed by inspecting the second derivatives matrix—the Hessian of the energy. The Hessian in the tridimite/cristobalite extremum breaks into two 2×2 blocks, one with respect to variables Ψ, R another with respect to ζ, ϑ . The latter reads:

$$\begin{pmatrix} E''_{\zeta\zeta} & E''_{\zeta\vartheta} \\ E''_{\vartheta\zeta} & E''_{\vartheta\vartheta} \end{pmatrix} = \begin{pmatrix} b & -a \\ -a & a - f - g \end{pmatrix}; \quad (25)$$

$$a > b > 0, \quad c < 0,$$

where

$$\begin{aligned} E''_{\zeta\zeta} &= b = c + d, \quad c < 0, \\ c &= 8(U_{pp}^O - U_{ss}^O) \sin^2 \Psi, \\ d &= 4\sqrt{2}B_\sigma (\sqrt{3}t_{\zeta\sigma}(R) + t_{\sigma\sigma}(R)), \\ E''_{\zeta\vartheta} &= E''_{\vartheta\zeta} = 4\sqrt{2}B_\sigma (\sqrt{3}t_{\zeta\zeta}(R) + t_{\sigma\zeta}(R)) = -a, \end{aligned} \quad (26)$$

$$E''_{\vartheta\vartheta} = a - f - g,$$

$$f = 3\Pi\Omega R^3 > 0,$$

$$g = \frac{2\kappa Q^2}{R} > 0.$$

¹³The derivative of the hydrostatic term vanishes at $R \rightarrow 0$ and is positive at $R \rightarrow \infty$; the derivative of the resonance terms in the 3rd row is positive at $R \rightarrow \infty$ and negative at $R \rightarrow 0$; thus the conclusion of the theorem does not change.

¹⁴We also notice that the reasoning in footnote 4 of [16] leading to an analogous result is wrong, although the conclusion is, of course, correct, as here.

¹⁵Indeed to the left from R_0 —at $R_0 - \delta$ —the derivative $f'(R_0 - \delta) < 0$ and to the right—at $R_0 + \delta$ — $f'(R_0 + \delta) > 0$, thus $\lim_{\delta \rightarrow 0} \frac{f'(R_0 + \delta) - f'(R_0 - \delta)}{2\delta} = f''(R_0) > 0$; and R_0 provides a minimum.

The analysis evolves as follows. First, we omit the terms proportional to κ and Ω —the global structure variables. Then, the simplified Hessian reads

$$\begin{pmatrix} b & -a \\ -a & a \end{pmatrix},$$

so that, according to the Sylvester criterion, the stability is lost as soon as $a(b - a) < 0$, namely as soon as $b - a < 0$. Including f, g —adding hydrostatic pressure or/and taking into account the long range interactions of the effective oxygen dipoles appearing upon bending of Si—O—Si bonds—shifts the system towards instability with respect to the bending. Nevertheless, fundamentally, the story of (in)stability turns around the relation between two short-range i.e., chemical: the constant negative intra-atomic term—the difference between the core attractions (U_{pp}^O and U_{ss}^O) on the s - and p -AOs of oxygen, and the positive component of the two-center σ -resonance parameter, however, decreasing with increasing R .

The tentative destabilizing effect of the second derivatives is compensated by that of the fourth ones (due to abovementioned symmetry Eq. (23) of the energy function Eq. (22) the odd derivatives with respect to ζ, ϑ vanish at the tridimite/cristobalite extremum). The trigonometric character of the involved functions, assures that the components of the fourth derivatives are proportional to the respective components of the second derivatives, namely:

$$\begin{pmatrix} E^{(iv)}_{\zeta\zeta\zeta\zeta} & E^{(iv)}_{\zeta\zeta\vartheta\vartheta} \\ E^{(iv)}_{\vartheta\vartheta\zeta\zeta} & E^{(iv)}_{\vartheta\vartheta\vartheta\vartheta} \end{pmatrix} = \begin{pmatrix} -4c - d & 0 \\ 0 & -a + 2g + 7f \end{pmatrix}$$

$$\approx \begin{pmatrix} -4c - d & 0 \\ 0 & -a \end{pmatrix}.$$

The energy near the tridimite/cristobalite extremum is approximately:

$$\begin{aligned} \tilde{E} &\approx \frac{1}{2}(c + d)\zeta^2 + \frac{1}{2}a\vartheta^2 - a\vartheta\zeta \\ &\quad - \frac{1}{24}(4c + d)\zeta^4 - \frac{1}{24}a\vartheta^4. \end{aligned}$$

Expressing ζ through ϑ from the condition:

$$\begin{aligned} \tilde{E}'_{\vartheta} &= a\vartheta - a\zeta - \frac{1}{6}a\vartheta^3 = 0, \\ \zeta &\approx \vartheta, \end{aligned}$$

we arrive to the effective bending potential for the $\text{O}_3\text{Si—O—SiO}_3$ joint:

$$\tilde{\tilde{E}} = \frac{1}{2}(b - a)\vartheta^2 - \frac{1}{24}(3c + b - a)\vartheta^4. \quad (27)$$

Analysis of the signs of the contributions to the coefficients at ϑ^2 and ϑ^4 shows that one at the fourth power is always positive, whereas the sign of the quadratic term may be either positive or negative depending on

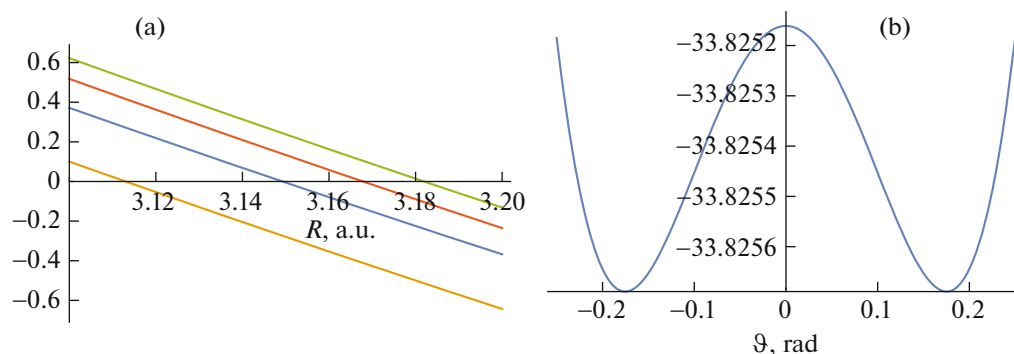


Fig. 8. (a) The Si–O distance dependence of the values of the Hessian determinant for different exemplary values of the Hessian contributions: blue $\kappa = 5$, $\Pi = 0$ GPa; orange $\kappa = 5$, $\Pi = 1$ GPa; green $\kappa = 4$, $\Pi = 0$ GPa; red $\kappa = 4$, $\Pi = 0$ GPa; $(U_{ss}^O - U_{pp}^O)$ increased by 1 eV. (b) The bending angle ϑ dependence of the energy of a tetrahedral polymorph beyond the instability threshold. For details of the parameterization used to obtain this graph see Appendix A.

the relation among the contributions Eq. (26) to the Hessian equation (25).

The derived model is rich enough. Depending on the contributions to the Hessian the values of its determinant are shown as functions of Si–O interatomic separation in Fig. 8a. Obviously, the extremum of the tridimite/cristobalite energy at $R_0 = 3.05$ a.u. lies close to the instability threshold. Taking into account the orders of magnitude of the thermal expansion coefficient α of tridimite of $\sim 10^{-4}$ K $^{-1}$ [5, 58], in the temperature range of ~ 1000 – 2000 K employed in the phase diagram Fig. 1, we see that the spread of the values of the Si–O separations $R \rightarrow R(1 + \alpha T)$ may reach $\sim 10\%$ so that with increasing temperature the value of R may shift towards larger values as compared to the equilibrium one (see below) which leads to the loss of stability of the linear configuration of the linear configuration of the $O_3Si-O-SiO_3$ units. This corresponds to a *displacive* transition: the form of the *potential* energy changes from a single minimum to one with multiple minima;¹⁶ the variable ϑ itself serves as the order parameter of the phase transition. The result of calculation of the potential energy of a tetrahedral polymorph as a function of bending angle ϑ above the instability threshold is depicted in Fig. 8b. Nevertheless, even beyond the instability threshold (in the high-temperature phase(s) of cristobalite and tridimite) the occupation of six equivalent positions, to which O atoms may slide, are the same so that the observed structure corresponds to the vanishing thermodynamic average $\langle \vartheta \rangle$. This may change upon an *order-disorder* phase transitions in tridimite/cristob-

alite [4]. The latter reduces to selection of only one of the equivalent sliding directions of the O atoms in the low-temperature cristobalite and tridimite phases driven by entropic terms. The order parameter of the *order-disorder* transition is the thermodynamic average $\langle \vartheta \rangle$ and in variance with the displacive transition the temperature variation in the vicinity of the critical temperature of the order-disorder transition affects the sign of the coefficient at $\langle \vartheta \rangle^2 (\neq \langle \vartheta^2 \rangle)$ —the square of its order parameter—in the expansion of the *free* energy and not of the potential one.

The bending amplitude is controlled by the precise value of the global structure parameter κ and may differ in different crystals. This possibly explains geometry even of quartz crystals featuring considerable values of the Si–O–Si bending angles. The form of the κ -dependent contribution to the energy Eq. (21) suggests that for larger values of κ *ceteris paribus* one may expect also larger equilibrium values of both effective charges Q and the bending amplitude ϑ . Remarkably, in the recent PAW/DFT calculation [59] of quartz accompanied by the LOBSTER [46–48] analysis of the electronic distribution the charge of the oxygen atom in quartz is -0.9 to be compared with our value -0.45 in tridimite/cristobalite. This also indicates a significant contribution of covalency to bonding. Nevertheless, we have to admit that an adequate description of larger deformations like those occurring in quartz may require to explicitly include further interactions of atoms beyond the SiO_4 tetrahedra as it is suggested in the context of the rigid units model (RUM) of “tetrahedral” polymorphs [60, 61]. We postpone this for future publications.

The simplest picture of not deformed SiO_4 tetrahedra, we followed throughout this paper, conforms to the models describing the variety of the SiO_2 low-pressure/density polymorphs in terms of RUM [60, 62,

¹⁶The double well potential of Fig. 8 (right) transforms to one with multiple minima as a function of the direction of the bending normal to the Si–O–Si axis. Such a modification of the potential energy can be inferred from analysis of the structure (see Fig. 2).

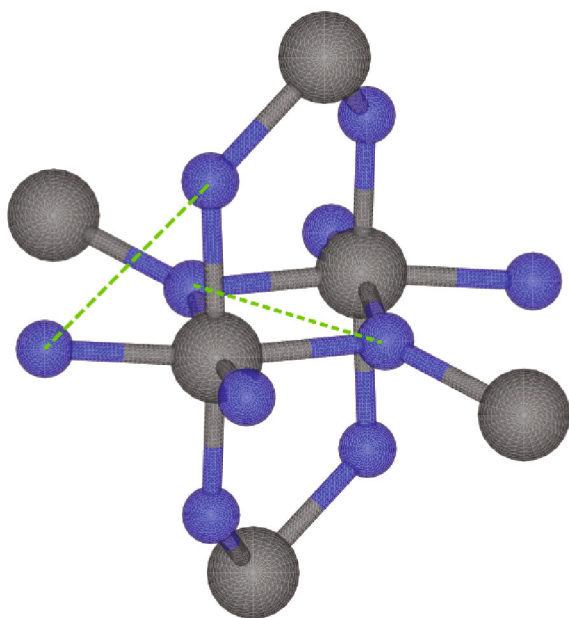


Fig. 9. Fragment of the seifertite structure. Coordination patterns of Si and O atoms are shown as well as shared edges (green dotted lines).

63]. It is known that in some cases the SiO_4 tetrahedra may slightly compress (e.g., in β -quartz) keeping the second order rotation axes of tetrahedra only. This type of deformation is orthogonal to the allowed deformations of the entire system of hybrids of the Si atoms [24, 25]. The above squeezing deformation does not change the interhybrid angles at least in the lowest order. That means that the ideal sp^3 -character of hybridization of the Si atom almost does not change under the squeezing, but this deformation produces some additional strain since the directions of the Si–O bonds do not exactly coincide with the directions of the Si HOs any more. Despite the described deformations the SiO_4 tetrahedra are very stable in the silica polymorphs. Even pretty-high pressure polymorph—coesite—retains them. In fact, coesite is formed by two layers of 4-membered rings of fairly ideal SiO_4 tetrahedra with two values of the Si–O–Si angles of 137.36° and 144.5° . Analytical description of such a phase requires too many additional geometry variables and is beyond the scope of this paper. Necessary analysis can be performed numerically in a more general scheme which allows for full optimization of all hybrids including those of the Si atom where of particular interest would be a transient deformation of the tetrahedra under increasing pressure, which appears in quartz and disappears in coesite. We shall address this elsewhere.

3.2. Analysis of Octahedral Silica Polymorphs

Here we extend our treatment of silica to its high-pressure “octahedral” polymorphs. The “tectonic” terms—the core-core repulsions and the effective charge attractions have fundamentally the same form as for “tetrahedral” polymorphs. The difference is due to the nearest neighbor surrounding—octahedral with shared two equatorial edges and tetrahedral, respectively. As in the case of “tetrahedral” polymorphs, the “tectonic” terms assure the existence of the minimum with respect to the Si–O separation R . Unlike in the “tetrahedral” polymorphs, where it refers to real tridimite/cristobalite structures, the energy minimum derived in the ideal octahedral geometry represents nothing except a useful starting point for further treatment.

The necessary equations can be found above and in Appendices A, B. The results are as follows. The Si–O interatomic separation comes out as $R = 3.114$ a.u. to be compared with 3.353 a.u.—the average of the experimental values of R_{ax} and R_{eq} characteristic for stishovite [11, 64–68]. Remarkably, in the denser rutile structure the Si–O interatomic separation is *larger* than in the looser tridimite/cristobalite in full agreement with experiment. The higher coordination numbers in the rutile-type structure allow a longer nearest neighbor separation reducing individual repulsive contributions.

Equilibrium values of the Φ, Ψ variables correspond to effective charge of oxygen atoms of $Q = -0.57$ as compared to $Q = -0.45$ in tridimite/cristobalite. We see that higher pressure phase is more ionic than the low pressure ones, but still retains a significant fraction of covalency. The optimal values of variables describing deformation of the SiO_6 octahedra in stishovite are $r = -0.001$ a.u., $\phi = -0.319 = (-18.31^\circ)$, $\zeta = 1.31$. The sign of r is wrong—microscopic shrinking of the axial bond instead of noticeable elongation, provided the microscopic absolute value any way incompatible with experimental observation, we conclude that it requires further consideration. The sign of angle ϕ is reproduced correctly; the numerical value is somewhat exaggerated (experimental value of -8.64°). The equilibrium value of the hybridization variable ζ corresponds to the angle of 114.9° between the equatorial hybrids (minimal accessible interhybrid angle is 90° which corresponds to $\zeta = \pi - \arctan \sqrt{2} \approx 2.186$). This indicates that in the equilibrium point of the proposed model the equatorial oxygen hybrids are closer to ideal sp^2 -hybrids than to pure atomic p -orbitals. At the same time the O–Si–O angle opposite to the shared edge amounts 98° showing the misfit of 8° between the directions of the hybrids and those of the bonds. These results are accessed at an equilibrium value of the $|a_i^{(+)}\rangle$ amplitude $\sin \varphi = 0.98$ (the weight

of 0.95) that is to say that the HOMO of the deformed CLS is almost completely the $|a_1^{(+)})$ one. In general, one can say that qualitatively the deformations of stishovite structure as compared to ideal one are reproduced although, numerically, agreement is far from perfect. Apparently, one cannot expect more in the setting where only *one* parameter is actually fitted (see Appendix A.2).

Looking at the structure of another high-pressure (high-coordination) silica polymorph—seifertite [64–66, 69, 70] (Fig. 9 we notice that locally it is pretty similar to stishovite: both feature $\text{CN}(\text{Si}) = 6$, $\text{CN}(\text{O}) = 3$ and, respectively, approximately octahedral and planar trigonal coordination. The octahedra in seifertite each share two of their edges with neighbor ones, but in variance with stishovite the shared edges in seifertite are not parallel, but lie in orthogonal planes (or in other words belong to skew straight lines). Further inspection reveals that the deviations of the local geometry of the SiO_6 octahedra in seifertite from the ideal one follow the t_{1u} symmetry (all three *trans*-O—Si—O angles amount 171° ; of three O—Si—O units two have unequal Si—O separations of 1.742 and 1.855 Å, whereas the third one keeps them equal at 1.776 Å; the coordination of oxygen atoms slightly deviates from strictly planar—the defect of 3° ; very remarkable is the finding that the Si—O—Si angle opposite to the shared edge amounts 97° —almost precisely coincides with the analogous value in stishovite). Electronic structure of so deformed octahedra can be described analogously to stishovite, namely, through an admixture of the $|a_1^{(+)})$ LUMO to the lower lying occupied $|t_{1u}^{(-)})$ MO of the ideal CLS. This will be addressed elsewhere.

4. CONCLUSION AND OUTLOOK

In the present paper we developed DMM models for two classes of silica polymorphs: low pressure/low coordinate “tetrahedral” ones exemplified by tridimite/cristobalite and the high-pressure/high coordinate “octahedral” ones exemplified by stishovite/seifertite. In either case descriptions based on the relevant models of electronic structures of respective electronic groups and including variables necessary to describe electronic structure of considered polymorphs are developed. The DMM model is explicitly constructed in terms of quantum mechanical entities and, thus, possesses certain explanatory force. Specifically, for tetrahedral low-density polymorphs the intimate nature of instability, of the linear configuration of the $\text{O}_3\text{Si—O—SiO}_3$ units, characteristic for low-coordinate polymorphs, with respect to the bending of the Si—O—Si bonds, namely, the interplay between the resonance (electron hopping) pushing towards larger involvement of oxygen *p*-AOs in the bonding HOs and the *s*—*p* energy gap ($U_{ss}^O - U_{pp}^O$) requiring a larger involve-

Table 3. Selected values of atomic parameters used throughout numerical experiments

	ξ^E	U_{ss}^E	U_{pp}^E	G^E
	Bohr ⁻¹	eV		
Si	1.383	36.494	30.375	6.964
O	2.275	101.306	84.28	13.625

ment of *s*-AOs in the nonbonding LP HOs of oxygen atoms. This relation, known for decades as the Bent rule [24, 71], but almost forgotten by now. This constitutes a prerequisite for possible displacive and/or order-disorder transitions eventually *explaining* the space of the low-density phases at the microscopic level. Some time ago it was shown that the low-pressure phases can be derived from the stishovite structure [70]. Our tentative alternative approach starts from the low-pressure symmetric phases tridimite/cristobalite and represents others as a consequence of Si—O—Si bendings of different magnitude and mutual arrangement.

As for the DMM model of stishovite (and eventually seifertite) in the frame of the “proof of a concept” setting the most characteristic structure features of this family of polymorphs are reproduced (for stishovite) paving a way for future developments in the realm of higher-pressure phases.

APPENDIX A

PARAMETERIZATION AND CALCULATION DETAILS

In the present paper devoted to a “proof of concept” the parameterization serves to obtain some illustrative material together with semiquantitative estimates of the orders of magnitude of the expected effects. Thus we employ the simplest possible parameterization scheme addressing only the basic physics. In the semiempirical quantum chemistry context the required set of parameters is implemented in the CNDO scheme [45]. For *sp*-atoms in involves the one-center parameters: one-electron core attraction on the *s*- and *p*-AOs (U_{ss}^E and U_{pp}^E) and two-electron Coulomb repulsion matrix elements G^E . The numerical values of these parameters for elements of 2nd and 3rd periods have been fitted in [72–75] assembled in Table 3.

A.1. Coulomb, Resonance, and Overlap Integrals

Two-center matrix elements as well classify in one- and two-electronic (Coulomb) ones. As we mentioned in Section 2.2.3 the Coulomb interaction terms are taken on the average—having the same values for different types of orbitals (*s* and *p*). The explicit expres-

sions of the Coulomb interactions $\gamma_{EE'}(R)$ Eq. (16) (following the same equation also for the core-core repulsions $Y_{EE'}(R)$) are quite tedious as described in [45]. They parametrically depend on the orbital exponents ξ^E of the Slater type AOs as well characteristic for each atom (see Table 3).

A.1.a. Interactions of effective charges and cores.

For the involved effective charges the O- ($-Q < 0$) and Si- ($2Q > 0$) atoms and the closest neighbors in “tetrahedral” polymorphs we simply rewrite the result for (symmetric) ice X [16]:

$$Q^2 [6\gamma_{OO}(\sqrt{8/3}R) - 8\gamma_{SiO}(R)]. \quad (A.1)$$

Analogously, for stishovite (rutile) the SiO_6 octahedra one needs to take into account the interactions along six Si–O bonds and along O–O edges. Two of the O–O edges in the equatorial plane are shared with the neighbor octahedra. Thus the contribution of these interactions needs to be taken into account only once per Si atom (or SiO_2 formula unit). In the “octahedral” polymorphs the nearest-neighbor interaction of effective charges is:

$$Q^2 \left[-2(2\gamma_{SiO}(R_{ax}) + 4\gamma_{SiO}(R_{eq})) + 8\gamma_{OO}(\sqrt{R_{ax}^2 + R_{eq}^2}) + \gamma_{OO} \left(2R_{eq} \sin \left(\frac{\pi}{4} + \frac{\phi}{2} \right) \right) + 2\gamma_{OO} \left(2R_{eq} \sin \left(\frac{\pi}{4} - \frac{\phi}{2} \right) \right) \right] \quad (A.2)$$

The term with the $\sin \left(\frac{\pi}{4} + \frac{\phi}{2} \right)$ multiplier in the argument refers to the shared equatorial edges of the SiO_6 octahedron (Fig. 4) and thus is accounted only once.

The “Yukawa” contribution (proportional to the product of core charges $Z_O = 6, Z_{Si} = 4$) reads:

$$96Y_{SiO}(R) + 216Y_{OO}(\sqrt{8/3}R) \quad (A.3)$$

for the “tetrahedral” polymorphs and

$$24(2Y_{SiO}(R_{ax}) + 4Y_{SiO}(R_{eq})) + 36 \left[8Y_{OO}(\sqrt{R_{ax}^2 + R_{eq}^2}) + Y_{OO} \left(2R_{eq} \sin \left(\frac{\pi}{4} + \frac{\phi}{2} \right) \right) + 2Y_{OO} \left(2R_{eq} \sin \left(\frac{\pi}{4} - \frac{\phi}{2} \right) \right) \right] \quad (A.4)$$

for the rutile structure. The latter reduces to:

$$144Y_{SiO}(R) + 396Y_{OO}(\sqrt{2}R) \quad (A.5)$$

for the ideal octahedron with two shared edges.

Expanding the both repulsion potentials at the ideal octahedral geometry ($r, \phi = 0$):

$$-\frac{36Y'_{OO}(\sqrt{2}R)R}{\sqrt{2}}\phi, \quad -\frac{Q^2\gamma'_{OO}(\sqrt{2}R)R}{\sqrt{2}}\phi$$

reveals the inherent preference for the negative values of the deformation parameter ϕ in the rutile structure.

A.1.b. Hybridization dependence of core attraction.

In “tetrahedral” polymorphs featuring two types of HO’s on the O-atoms, respectively, belonging to LPs and σ -bonds the weights of the s -AOs Eq. (5) yield:

$$U_{\lambda}^O = \frac{U_{ss}^O + U_{pp}^O}{2} - \frac{U_{ss}^O - U_{pp}^O}{2} \cos^2 \zeta,$$

$$U_{\sigma}^O = U_{pp}^O + \frac{U_{ss}^O - U_{pp}^O}{2} \cos^2 \zeta$$

for the lone pair and σ -bonding HO, respectively. The resulting energy contribution reads:¹⁷

$$-4(U_{ss}^O + U_{pp}^O) - 8P_{\sigma}U_{pp}^O + 4(1 - P_{\sigma})(U_{ss}^O - U_{pp}^O) \cos^2 \zeta. \quad (A.6)$$

This needs to be taken *twice* for two O-atoms in the SiO_2 formula unit.

In the “octahedral” polymorphs O-atoms feature deformed sp^2 -hybridization. Of four O-HOs one is doubly occupied pure p -AO (LP). Next, six Si–O separations within octahedra are subdivided into two longer ones: axial, and four shorter ones: equatorial. One of the sp^2 -O-HO’s is oriented along the axial Si–O bond, whereas two others along the equatorial Si–O bonds of the other Si-atoms (Fig. 4). Since the lengths of the Si–O bonds are different, the HO’s ascribed to them and the core attraction parameters for the axial and equatorial HO’s as well differ:

$$\left. \begin{matrix} U_{ax}^O \\ U_{eq}^O \end{matrix} \right\} = \frac{1}{3} \left[(2U_{pp}^O + U_{ss}^O) + (U_{ss}^O - U_{pp}^O) \right] \quad (A.7)$$

$$\times (\sin^2 \zeta - 2\sqrt{2} \cos \zeta \sin \zeta) \left\{ \begin{matrix} 1 \\ -1/2 \end{matrix} \right. \quad (A.8)$$

For the symmetric octahedron ζ has to be set equal to zero, so that the ζ -dependent terms disappear; otherwise they serve as components of the perturbation Eq. (14) of the CLS Fock operator (see below). In the symmetric case the energy of the core attraction of electrons in O-atoms yields altogether the contribution of:

$$-4U_{pp}^O - 4P_{lp}(2U_{pp}^O + U_{ss}^O).$$

The core attraction in Si atoms is much simpler either in “tetrahedral” or “octahedral” setting. For the sp^3 hybridized Si atom in tetrahedral polymorphs the core attraction contribution reads:

$$-2(1 - P_{\sigma})(U_{ss}^{Si} + 3U_{pp}^{Si}).$$

¹⁷Populations are calculated for one spin projection, thus, need to be multiplied by two, and this applies to two hybrids of each type—bonding and LP HO’s, respectively.

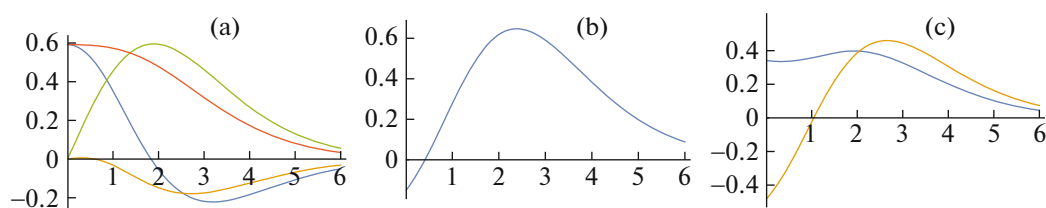


Fig. 10. Overlaps as functions of R for the left atom Si and right atom O. (a) Individual overlaps: $S_{\zeta\zeta}^{\text{SiO}}$ —blue, $S_{\sigma\zeta}^{\text{SiO}}$ —orange, $S_{\zeta\sigma}^{\text{SiO}}$ —green, $S_{\sigma\sigma}^{\text{SiO}}$ —red. (b) The overlap between ideal sp^3 -Si (left-end) and sp -O (right-end). (c) Overlaps, respectively (blue and orange), between the s - and p -AOs of Si and axial sp^2 -oxygen HOs.

In the “octahedral” environment of Si no hybridization is necessary, thus for the core attraction we simply write

$$-2U_{ss}^{\text{Si}}P_s - 6U_{pp}^{\text{Si}}P_p.$$

The core attraction terms demonstrate an important interplay between the involved variables. These terms are always negative—stabilizing, however, the core attraction for oxygen is much stronger than for silicon driving towards more ionic—larger populations P_σ , P_p of the oxygen bonding HO—and through the normalization of the number of electrons in each group—to smaller populations of Si HOs. Remarkably, in tetrahedral polymorphs the oxygen core attraction Eq. (A.6) is hybridization dependent. It is maximal when the s -contribution to the bonding HO is maximal, i.e. in the linear sp -hybridization. Stronger core attraction leads to larger ionicity—increase of P_σ . However, increasing of P_σ —polarity of the Si—O bond damps the hybridization dependence: at $P_\sigma = 1$ —purely ionic bond—the ζ -dependent contribution disappears and the hybridization has no effect. This is not surprising: the *state* of an atom (ion) with completely filled valence shell (isoelectronic to noble gases) is spherically symmetric.

A.1.c. Resonance matrix elements. The most sophisticated interaction function is the resonance interaction matrix element. According to Eq. (17), the resonance matrix elements between HOs are expressed through the respective matrix elements between AOs. Within CNDO these latter have the form:

$$t_{\mu\nu}^{\text{SiO}}(R) = \beta^{\text{SiO}} S_{\mu\nu}^{\text{SiO}}(R); \quad \mu, \nu = \sigma, \zeta, \pi,$$

where β^{SiO} is a energy scaling factor, and $S_{\mu\nu}^{\text{SiO}}$ are the overlap integrals between Slater AOs with the exponents given in Table 3.

Corresponding graphs are given in Fig. 10. For the ideal arrangement of the O atoms in the SiO_4 tetrahedra we take the Si—Si line for the x -axis and a perpendicular to it going through the O atom for the y -axis.

z -axis is then the normal to the xy - (SiOSi) plane. In this coordinate frame the Si—O bond vector reads:

$$\vec{e}_{\text{SiO}} = (\cos \vartheta, \sin \vartheta, 0).$$

With use of the trigonometric parametrization Eq. (5) we get for the bonding hybrids:

$$\begin{aligned} (s^{\text{O}}, \vec{v}^{\text{O}}) &= \frac{1}{\sqrt{2}}(\cos \zeta, -1, -\sin \zeta, 0), \\ s^{\text{Si}} &= \frac{1}{2}, \quad \vec{v}^{\text{Si}} = \frac{\sqrt{3}}{2}\vec{e}_{\text{SiO}}. \end{aligned} \quad (\text{A.9})$$

Taking the axial bond for the positive direction of the z -axis the hybrids can be written:

$$\begin{aligned} \text{ax:} \quad & \left(\frac{1}{\sqrt{3}}\cos \zeta - \sqrt{\frac{2}{3}}\sin \zeta \right) |s\rangle \\ & - \left(\sqrt{\frac{2}{3}}\cos \zeta + \frac{1}{\sqrt{3}}\sin \zeta \right) |z\rangle, \\ \text{eq:} \quad & \frac{1}{\sqrt{2}} \left[\left(\sqrt{\frac{2}{3}}\cos \zeta + \frac{1}{\sqrt{3}}\sin \zeta \right) |s\rangle \pm |x\rangle \right. \\ & \left. + \left(\frac{1}{\sqrt{3}}\cos \zeta - \sqrt{\frac{2}{3}}\sin \zeta \right) |y\rangle \right]. \end{aligned} \quad (\text{A.10})$$

With this, the weights of the s -AOs in the respective hybrids are:

$$\frac{1}{3} + \frac{1}{3} \begin{cases} \sin^2 \zeta - 2\sqrt{2}\cos \zeta \sin \zeta & \text{ax} \\ -\frac{\sin^2 \zeta}{2} + \sqrt{2}\cos \zeta \sin \zeta & \text{eq}, \end{cases} \quad (\text{A.11})$$

and the cosine of the angle between the equatorial hybrids is given by:

$$\frac{1 - \frac{1}{2}\sin^2 \zeta + \sqrt{2}\sin \zeta \cos \zeta}{2 + \frac{1}{2}\sin^2 \zeta - \sqrt{2}\sin \zeta \cos \zeta},$$

yielding two limiting cases: at $\zeta = 0$ the angle of $\frac{2\pi}{3}$ characteristic for the ideal sp^2 -hybridization, and at $\zeta = \pi - \arctan \sqrt{2}$ refers to the interhybrid angle of $\frac{\pi}{2}$

between pure p -AO's potentially conforming with the ideal octahedron geometry of SiO_6 .

In the octahedral setting the resonance integrals classify into sp^2 -axial and sp^2 -equatorial ones. For the axial ones we have

$$\begin{aligned}\vec{e}_{\text{SiO}} &= (0, 0, 1), \\ s_s^{\text{Si}} &= 1, \quad \vec{v}_p^{\text{Si}} = \vec{0}, \\ s_p^{\text{Si}} &= 0, \quad \vec{v}_p^{\text{Si}} = \vec{e}_{\text{SiO}},\end{aligned}$$

where from we get

$$\begin{aligned}t_{s,lp}^{\text{ax}}(R, r, \varsigma) &= \frac{1}{\sqrt{3}} \left[t_{\sigma\sigma}(R + 2r) (\cos \varsigma - \sqrt{2} \sin \varsigma) \right. \\ &\quad \left. - t_{\sigma\zeta}(R + 2r) (\sin \varsigma + \sqrt{2} \cos \varsigma) \right], \\ t_{p,lp}^{\text{ax}}(R, r, \varsigma) &= \frac{1}{\sqrt{3}} \left[t_{\zeta\sigma}(R + 2r) (\cos \varsigma - \sqrt{2} \sin \varsigma) \right. \\ &\quad \left. - t_{\zeta\zeta}(R + 2r) (\sin \varsigma + \sqrt{2} \cos \varsigma) \right].\end{aligned}$$

For the equatorial ones:

$$\begin{aligned}\vec{e}_{\text{SiO}} &= \left(\cos\left(\frac{\pi}{4} - \frac{\phi}{2}\right), \sin\left(\frac{\pi}{4} - \frac{\phi}{2}\right), 0 \right), \\ s_p^{\text{Si}} &= 0, \quad \vec{v}_p^{\text{Si}} = \frac{1}{\sqrt{2}}(1, 1, 0),\end{aligned}$$

and

$$\begin{aligned}t_{s,lp}^{\text{eq}}(R, r, \varsigma, \phi) &= \frac{1}{6} \left[\sqrt{3} t_{\sigma\sigma}(R - r) (\sqrt{2} \sin \varsigma + 2 \cos \varsigma) \right. \\ &\quad \left. + t_{\sigma\zeta}(R - r) \left(\cos \frac{\phi}{2} (\sqrt{6} \sin \varsigma - \sqrt{3} \cos \varsigma - 3) \right. \right. \\ &\quad \left. \left. + \sin \frac{\phi}{2} (\sqrt{6} \sin \varsigma - \sqrt{3} \cos \varsigma + 3) \right) \right], \\ t_{p,lp}^{\text{eq}}(R, r, \varsigma, \phi) &= \frac{t_{\zeta\sigma}(R - r)}{2\sqrt{3}} \cos \frac{\phi}{2} (\sqrt{2} \sin \varsigma + 2 \cos \varsigma) \\ &\quad + \frac{t_{\zeta\zeta}(R - r)}{12} \left[\sqrt{6} \sin \phi \sin \varsigma - \sqrt{3} (\sin \phi + 1) \cos \varsigma \right. \\ &\quad \left. + \cos \phi (\sqrt{6} \sin \varsigma - \sqrt{3} \cos \varsigma - 3) \right. \\ &\quad \left. + 3 \sin \phi + \sqrt{6} \sin \varsigma - 3 \right] \\ &\quad + \frac{t_{\pi\pi}(R - r)}{12} \left[-\sqrt{6} \sin \phi \sin \varsigma + \sqrt{3} (\sin \phi - 1) \cos \varsigma \right. \\ &\quad \left. + \cos \phi (-\sqrt{6} \sin \varsigma + \sqrt{3} \cos \varsigma + 3) \right. \\ &\quad \left. - 3 \sin \phi + \sqrt{6} \sin \varsigma - 3 \right].\end{aligned}$$

One can check that the values of $t_{s,lp}^{\text{ax}}$, $t_{s,lp}^{\text{eq}}$ and $t_{p,lp}^{\text{ax}}$, $t_{p,lp}^{\text{eq}}$, respectively, coincide for $r = \varsigma = 0$; $\phi = -\frac{\pi}{6}$. These values are employed for constructing the symmetrized CLS of the Si atom in stishovite. The difference between the values at $r = \varsigma = 0$; and the at the actual values of r, ς, ϕ contribute to the perturbation Eq. (14), which takes the matrix form:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \delta\beta_{s,lp}^{\text{eq}} & \delta\beta_{s,lp}^{\text{eq}} & \delta\beta_{s,lp}^{\text{eq}} & \delta\beta_{s,lp}^{\text{eq}} & \delta\beta_{s,lp}^{\text{ax}} & \delta\beta_{s,lp}^{\text{ax}} \\ 0 & 0 & 0 & 0 & \delta\beta_{p,lp}^{\text{eq}} & -\delta\beta_{p,lp}^{\text{eq}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \delta\beta_{p,lp}^{\text{eq}} & -\delta\beta_{p,lp}^{\text{eq}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \delta\beta_{p,lp}^{\text{ax}} & -\delta\beta_{p,lp}^{\text{ax}} \\ \delta\beta_{s,lp}^{\text{eq}} & \delta\beta_{p,lp}^{\text{eq}} & 0 & 0 & -\frac{\Delta_{sp}}{2} & 0 & 0 & 0 & 0 & 0 \\ \delta\beta_{s,lp}^{\text{eq}} & -\delta\beta_{p,lp}^{\text{eq}} & 0 & 0 & 0 & -\frac{\Delta_{sp}}{2} & 0 & 0 & 0 & 0 \\ \delta\beta_{s,lp}^{\text{eq}} & 0 & \delta\beta_{p,lp}^{\text{eq}} & 0 & 0 & 0 & -\frac{\Delta_{sp}}{2} & 0 & 0 & 0 \\ \delta\beta_{s,lp}^{\text{eq}} & 0 & -\delta\beta_{p,lp}^{\text{eq}} & 0 & 0 & 0 & 0 & -\frac{\Delta_{sp}}{2} & 0 & 0 \\ \delta\beta_{s,lp}^{\text{ax}} & 0 & 0 & \delta\beta_{p,lp}^{\text{ax}} & 0 & 0 & 0 & 0 & \Delta_{sp} & 0 \\ \delta\beta_{s,lp}^{\text{ax}} & 0 & 0 & -\delta\beta_{p,lp}^{\text{ax}} & 0 & 0 & 0 & 0 & 0 & \Delta_{sp} \end{pmatrix},$$

where

$$\Delta_{sp} = \frac{1}{3}(U_{ss} - U_{pp})(\sin^2 \zeta - 2\sqrt{2} \cos \zeta \sin \zeta),$$

$$\delta\beta_{s,lp}^{\text{ax}} = -\left(t_{s,lp}^{\text{ax}}(R, r, \zeta) - t_{s,lp}^{\text{ax}}(R, 0, 0)\right) + B_s(\gamma_{\text{OE}}(R) - \gamma_{\text{OE}}(R + 2r)),$$

$$\delta\beta_{s,lp}^{\text{eq}} = -\left(t_{s,lp}^{\text{eq}}(R, r, \zeta, \phi) - t_{s,lp}^{\text{eq}}(R, 0, 0, 0)\right) + B_s(\gamma_{\text{OE}}(R) - \gamma_{\text{OE}}(R - r)),$$

$$\delta\beta_{p,lp}^{\text{ax}} = -\left(t_{p,lp}^{\text{ax}}(R, r, \zeta) - t_{p,lp}^{\text{ax}}(R, 0, 0)\right) + B_p(\gamma_{\text{OE}}(R) - \gamma_{\text{OE}}(R + 2r)),$$

$$\delta\beta_{p,lp}^{\text{eq}} = -\left(t_{p,lp}^{\text{eq}}(R, r, \zeta, \phi) - t_{p,lp}^{\text{eq}}(R, 0, 0, 0)\right) + B_p(\gamma_{\text{OE}}(R) - \gamma_{\text{OE}}(R - r)).$$

Upon substitution in the expressions Eqs. (9), (13) this yields the explicit form of the energy correction

$$\sin^2 \varphi (\epsilon_{a_1}^{(+)} - \epsilon_{e_g}) + \sin 2\varphi \left[\frac{2 \cos \Phi}{\sqrt{3}} (\delta\beta_{s,lp}^{\text{ax}} - \delta\beta_{s,lp}^{\text{eq}}) + \frac{\sin \Phi}{\sqrt{2}} \Delta_{sp} \right],$$

which is used in numerical experiments.

A.2. Details of Numerical Experiments

With the parameters listed in Table 3 and the reduced Madelung constant $\mu = 0.114$ characteristic for tridimite we minimized the energy Eq. (24) against R . The value of the resonance scaling parameter $\beta^{\text{SiO}} = 54.1 \text{ eV} \approx 2 \text{ a.u.}$ is adjusted so that the equilibrium Si–O distance coincides with the experimental one in tridimite. So obtained value is subsequently used in calculations.

APPENDIX B

CLS FOCKIAN COMPONENTS

The elements of the symmetrized Fockian Eq. (8) of the Si CLS are defined as:

$$\alpha_s = -U_{ss}^{\text{Si}} + G^{\text{Si}}(P_s + 6P_p) - \frac{MQ}{2R},$$

$$\alpha_p = -U_{pp}^{\text{Si}} + G^{\text{Si}}(2P_s + 5P_p) - \frac{MQ}{2R},$$

$$\alpha_{lp} = -\frac{2U_{pp}^{\text{O}} + U_{ss}^{\text{O}}}{3} + G^{\text{O}}(2 + 5P_p) + \frac{MQ}{2R},$$

$$\beta_{s,lp} = -(t_{s,lp} + B_s \gamma_{\text{OE}}),$$

$$\beta_{p,lp} = -(t_{p,lp} + B_p \gamma_{\text{OE}}),$$

where oxygen charge $Q < 0$.

The eigenvectors of the Fockian belong to definite symmetries so that the eigenvalues come either as solutions of square equations or simply the diagonal element of the symmetry adapted Fockian. Thus they can be explicitly written:

$$\epsilon_{e_g} = \alpha_{lp},$$

$$\epsilon_{a_1}^{(+)} = \frac{\alpha_s + \alpha_{lp}}{2} + \sqrt{\left(\frac{\alpha_s - \alpha_{lp}}{2}\right)^2 + 6\beta_{s,lp}^2},$$

$$\epsilon_{a_1}^{(+)} - \epsilon_{e_g} = \frac{\alpha_s - \alpha_{lp}}{2} + \sqrt{\left(\frac{\alpha_s - \alpha_{lp}}{2}\right)^2 + 6\beta_{s,lp}^2}$$

and employed in the calculations.

ACKNOWLEDGMENTS

This work is performed within the State task 122011300053-8 of the Russian Federation, “Surface phenomena in dispersed and colloidal systems; physico-chemical mechanics, adsorption and chromatographic processes”. The author gratefully acknowledges valuable discussions with Prof. Dr. A.V. Yatsenko and Dr. A.V. Larin (Moscow), Dr. I.O. Kitov (Vienna) and Prof. Dr. A.Y. Zakharov (Velikii Novgorod).

CONFLICT OF INTEREST

The author declare that he has no conflicts of interest.

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