High-pressure twisting of tetrahedra and amorphization in α -quartz

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It is discovered that the major contribution to the distortions of the tetrahedra in the α -quartz at high pressure is their twisting. It is shown that just these twisting vibrational modes lead to instability resulting in amorphization of the structure. [S0163-1829(99)00745-6]

Recently, a large number of computer simulations of the α -quartz structure at high pressures have been made.¹⁻⁶ Significant distortions of SiO₄ tetrahedra should be taken into account in these simulations when the relations between various microscopic parameters become numerous and complex. In this case, it is difficult to understand what sort of structure transformations are responsible for the dominant mechanisms of tetrahedral deformation. In order to clarify these mechanisms, we propose a simple valence force model, in which only two order parameters, most sensitive to pressure, have been distinguished. The tilt angle of SiO₄ tetrahedra is one of the two parameters, which was detected previously. It is commonly used to describe $\alpha - \beta$ phase transition of quartz.⁷ This angle is the main parameter of structure deformation at high pressure, and it is assumed to lead to instability, resulting in amorphization.^{8,9} We have found the second parameter, carefully analyzing numerous parameters of tetrahedral distortions, mentioned in the literature. We have discovered that these parameters can be reduced to a single parameter, i.e., the twist angle of tetrahedra. Earlier this angle was not considered as the order parameter at high pressures. The twist angle of tetrahedra can be defined as deviation from a 90° angle between two opposite symmetrical tetrahedron edges in α -quartz. As a result, we have managed to reveal some peculiarities, unnoticed in numerical calculations, i.e., the tilt angle at high pressures tends to saturation; the twist angle, on the other hand, starts to change nonlinearly. Therefore this is the angle which is mainly responsible for structure instability. This information seems to be important; despite a considerable quantity of experimental observations and theoretical simulations of α -quartz amorphization at high pressure,¹⁻¹² there is no correct description of the microscopic origin of the softening of the phonon modes, which are responsible for the elastic instability for reasons which are further discussed.

Earlier developed models aimed at explanation of hightemperature anomalies^{13–16} cannot be used for the description of the process of α -quartz amorphization, as they do not take into account essential tetrahedra distortions. The parameters, related to the least force constants and, consequently, readily varying with pressure, play the main role in the proposed valence force model of α -quartz deformation in which the tetrahedra distortions are taken into account. For example, if we speak about the main force constants, we should bear in mind that Si-O bond constant is significantly greater than O-Si-O angles force constant. The latter is significantly greater than Si-O-Si angle force constant. Therefore as the key parameters in our model we use the tilt angle, which is related to the Si-O-Si angle force constant and the twist angle, which is responsible for the deformation inside the tetrahedra and is related to the O-Si-O angles force constant. For the full description of the quartz structure it is necessary to introduce four more parameters, i.e., two symmetrical O-Si-O angles and two lengths of Si-O bonds. According to the experimental data, these four parameters at high pressures slightly change with increasing pressure,¹⁷ thus they are considered to be constant. All the parameters are relative and measured from the parameters of ideal β -quartz when Si-O distance is equal to 1.599 Å . The calculation on the available experimental structural data¹⁷ shows the tilt angle φ at pressures higher than 3 GPa to be 100 times greater than the four above-mentioned parameters. The twist angle τ , describing the tetrahedra distortion, is about ten times greater than these four small parameters. Therefore we will describe the tetrahedra distortions only using the twist angle.

Only one tilt angle is commonly used to construct an analytical deformation model of the quartz structure.^{7,13} Now let us consider the Gibbs potential, which takes into account both the twist angle and the tilt angle:

$$G = 3K_{\theta} [(\theta_0 - \theta) - (\theta_0 - \theta_m)]^2 + 3K_s \tau^2 + (P_{\alpha} + P)v,$$
(1)

where $v = (V - V_0)/V_0$ is a relative change of the volume of an elementary cell, θ is Si-O-Si angle, K_{θ} and K_s are force constants (in GPa) of Si-O-Si and O-Si-O angles, respectively. Here we have neglected small nondiagonal force constants. P_{α} is the internal pressure, which isothermally transfers β -quartz structure into α -quartz structure.¹⁸ This potential takes into account the tense state of the structure of ideal β -quartz. It is due to the fact that Si-O-Si angle, at which deformation is lacking, should be $\theta_m = 147^\circ$, but actually, the corresponding angle in the ideal β -quartz is θ_0 = 155.6°. Using v and θ expansions into φ and τ parameters we obtain the Gibbs potential, in which the variable part is as follows:

$$\Delta G = K_{\tau} \tau^2 / 2 + K_{\varphi} \varphi^2 / 2 - g_1 \tau + g_2 \tau \varphi^2 + g_4 \varphi^4, \qquad (2)$$

where all the coefficients are the pressure linear functions. The equilibrium values φ and τ for the minimum of this potential are equal to

$$\varphi = \left[\left(-K_{\varphi} - 2g_1 g_2 / K_{\tau} \right) / \left(4g_4 - 2g_2^2 / K_{\tau} \right) \right]^{1/2}, \qquad (3)$$

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FIG. 1. Pressure dependence of the tilt angle φ of SiO₄ tetrahedra of α -quartz calculated by Eq. (3). The squares represent experimental data (Ref. 17); the coordinates of silicon and oxygen for the trigonal quartz at higher pressures have not been determined yet (Ref. 19).

$$\tau = (g_1 - g_2 \varphi^2) / K_{\tau}.$$
 (4)

Let us construct the dependences $\varphi(P)$ and $\tau(P)$, shown in Figs. 1 and 2, using these equations. Analyzing the dependence $\varphi(P)$ at high pressures we obtain that it tends to saturation due to the contribution of the coefficient g_4 , which linearly increases with pressure. Earlier, based on the experimental data¹⁷, this saturation was supposed to exist, but it has not been explained. It should be noted that the tilt angle saturation with rise of pressure is connected with increasing the effective stiffness $K^*_{\varphi\varphi} = \partial^2 \Delta G / \partial \varphi^2$; this fact evidences that the structure stability increases and cannot be related to initiation of instability. It is evident from the dependence $\tau(P)$ that the twist angle of the tetrahedra starts to grow nonlinearly at high pressures, consequently, the effective stiffness $K^*_{\tau\tau} = \partial^2 \Delta G / \partial \tau^2 = K_{\tau}$ of the twist angle decreases. In this case, some elastic constants decrease, and the insta-



FIG. 2. Pressure dependence of the twist angle τ of SiO₄ tetrahedra of α -quartz calculated by Eq. (4). The squares represent experimental data (Ref. 17). The circle at 22 GPa corresponds to the average twist angle τ_{A1} for the triclinic phase, calculated by the structural data (Ref. 22). The dashed line corresponds to linear dependence.

bility, which initiates the disordered structure, can occur. Therefore the SiO₄ tetrahedra are no longer to be considered as quasisolid since the intrinsic twisting vibrations with high amplitudes become possible. In order to check this assumption, the calculations of the lattice dynamics have been carried out. They have been made not with the use of interatomic potentials, as usual, but with the help of the valence force field. This approach makes it possible to obtain the dependence of the force constants on pressure in the explicit form. The force field of α -quartz crystal is described in Ref. 20 using the scaled force constants $K_{qi,qj}^0$ of molecular silicate clusters, calculated by quantum-chemical methods.

In our calculations, we have used the above force constants. The second derivatives of the term Pv in the Gibbs potential with respect to the normal coordinates q_i in the vicinity of atom equilibrium positions, defined by the parameters $\varphi(P)$ and $\tau(P)$ from Eqs. (3) and (4), were added for taking the pressure into account. A similar procedure has been made in Ref. 21. As a result, the effective stiffnesses of the normal coordinates, depending on the pressure $K_{qi,qj}^*$ $=K_{qi,qj}^{0}+P(\partial^{2}V/\partial q_{i}\partial q_{j})$, have been obtained. The calculation of the low-frequency transverse-acoustical mode along the direction $[\xi, \xi, 0]$ in the Brillouin zone has been made using both these effective stiffnesses and the matrix of kinematic coefficients, which changes with pressure. It appeared that the acoustical wave velocity close to the Γ point is determined by the twist stiffness $v \propto (K^*_{\tau_{E1},\tau_{E1}})^{1/2}$ (where the parameter τ_{E_1} is further discussed) and tends to zero as pressure increases. The form of these soft acoustical vibrational modes results from the interaction of the twist optical transverse wave, in which oxygen atom displacements are mainly involved, and the acoustical transverse wave, in which silicon atoms are mainly displaced. Such softening can cause the rise of imaginary frequencies of the twist vibrational modes and, consequently, the loss of the tetrahedra stability with respect to twisting and, finally, to amorphization.

It has been recently emerged that according to experimental¹⁹ and theoretical²² data, the triclinic phase is formed before amorphization at 21 GPa. The calculation of coordination of atoms in this phase has shown that one of the three silicon atoms of a cell has fivefold coordination by oxygen, which is very close to that described in Ref. 23. Thus, in the triclinic transition, the transfer of a part of silicon atoms into the fivefold-coordinated site takes place. The above-described twisting vibrations in the soft modes can precisely lead to this kind of transition.

Let us explain what parameters are responsible for the transition into the triclinic phase. Each of the three tetrahedra of an α -quartz cell has one degree of freedom related to twisting. Three degrees of freedom cause various twistings τ_1 , τ_2 , τ_3 of three tetrahedra in an α -quartz cell, which brings about the formation of the three twisting parameters $\tau_{A_1} = (\tau_1 + \tau_2 + \tau_3)/3$, $\tau_{E_1} = (\tau_2 - \tau_1)/2$ and $\tau_{E_2} = \tau_3 - \tau_1/2 - \tau_2/2$ with statical and dynamical components. The statical part defines the equilibrium structural parameters, and the dynamical part—the vibrations near these equilibrium positions, which contribute with a certain amplitude to the normal crystal modes. The statical part of the average angle τ_{A_1} was earlier defined as twisting. The statical parts of τ_{E_1} and

 τ_{E_2} are zero in α -quartz and different from zero at the triclinic phase. The calculations made, using the structural data for the triclinic phase,²² show that τ_{E_1} is the main twisting parameter. This parameter provides an equal increase of the angle τ_2 and decrease of the angle τ_1 , so that the value of the average angle continues to fall on the curve of Fig. 2. Among the soft modes, which cause transition to the triclinic phase, there are sheared modes, which break symmetry. Twisting vibrations of *E* type significantly contribute to these modes. There are also longitudinal modes, responsible for the volume deformation of a cell, wherein the twisting vibrations of A_1 type make a contribution. The transition to the triclinic phase significantly strengthens the process of amorphization, because due to the break of symmetry, the twisting parameter τ_{A_1} contributes both to the volume and the shear moduli and significantly weakens it. With further increase of the pressure above 21 GPa, amorphization of this high-pressure triclinic structure occurs. Provided that generation of the amorphous phase is detected using the x-ray analysis even at pressures close to 15 GPa,⁸ the transition to the triclinic structure may be viewed as an intermediate stage in amorphization.

Thus we believe that the models, which do not take the distortions of the tetrahedra into account, are incorrect. For example, in Refs. 3–5, the soft phonon modes in α -quartz are related to the transition of silicon cation from tetrahedral to octahedral site in the oxygen body-centered-cubic lattice. In this case the angle between two opposite symmetrical tetrahedron edges in α -quartz is unchanged and it is equal to 90° . Thus, by definition, the twist angle does not change during this transformation and it remains equal to zero, whereas the experimental data¹⁷ in Fig. 2 show that the twist angle linearly increases with pressure up to 11 GPa. Furthermore, as the pressure increases up to 21 GPa, the twist angle additionally grows, because α -quartz transforms into a triclinic structure with highly distorted SiO₄ tetrahedra as observed in the experiments¹⁹ and theory.²² Besides, according to the estimations in Refs. 3 and 24, this hypothetical oxygen body-centered-cubic cell of quartz can be obtained only at high pressures ~ 80 GPa. In this connection it is believed that an increase of silicon coordination is due to the twisting vibrations of SiO_4 tetrahedra.

In a similar spirit, it is stated in a recent work²⁵ that α -quartz amorphous phase is obtained by the mechanism predicted by Stolper and Ahrens.⁹ In Ref. 9 it is considered the change of the tilt (rotation) angles of hard regular tetrahedra, i.e., Si-O-Si angles between adjacent tetrahedra. In this case the twist angle is not considered as before. We also state above that tilt angle of tetrahedra at high pressures tends to saturation (see Fig. 1) and, consequently, the effective stiffness of the structure, relative to that angle, increases. This fact evidences for the increase of the structure stability, and this cannot be related to the development of instability. Thus we suppose that the Stolper and Ahrens mechanism cannot lead to the amorphization of α -quartz structure. We believe that a gradual increase of silicon coordination and amorphization, observed in Ref. 25, occurs not with the help of the Stolper and Ahrens mechanism, but with the help of twist modes of SiO_4 tetrahedra. On this basis, we believe that our model is more realistic than the models mentioned above.

In conclusion it may be said that the valence force model of α -quartz deformation with good allowance for the tetrahedra distortion is proposed. In this model we choose the twist angle of tetrahedra as an order parameter. According to this model, the tetrahedra tilt angle tends to be saturated at high pressures and, consequently, the effective stiffness of the structure, relative to that angle, increases. This fact evidences for the increase of the structure stability and cannot lead to instability. At the same time, the parameter, lesser in magnitude, i.e., the twist angle, starts to grow nonlinearly with pressure. Therefore the SiO₄ tetrahedra at high pressures are no longer to be considered as quasisolid since the intrinsic twisting vibrations with the high amplitudes become possible. This causes softening of the lowest acoustical branch and loss of the tetrahedra stability, relative to twisting, thus causing transition into the triclinic phase with the subsequent structure amorphization.

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