

## Twisting of $\alpha$ -quartz tetrahedra at pressures near the transition to the amorphous state

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It is found that the main contribution to the distortion of  $\alpha$ -quartz tetrahedra at high pressures is their twisting. It is shown that torsional vibrational modes lead to an instability that gives rise to amorphization of the structure. © 1999 American Institute of Physics. [S0021-3640(99)00806-3]

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Many computer calculations of the structure of  $\alpha$ -quartz at high pressures have been performed in the last few years.<sup>1–4</sup> Such calculations take account of the distortion of the tetrahedra, such that the interactions between various structural parameters become numerous and complicated and the particular parameters responsible for the basic mechanisms leading to the deformation of the structure remain obscure. To determine these mechanisms we propose a simple valence-force model in which only the two structural parameters that are most pressure-sensitive stand out. One such parameter was found in previous work — the rotation angle of the SiO<sub>4</sub> tetrahedra, which is usually employed for describing the  $\alpha$ – $\beta$  transition in quartz.<sup>5</sup> This angle is the main parameter of the deformation of the structure at high pressures, and it is thought that it can lead to an instability that gives rise to amorphization.<sup>6</sup> We have found another parameter by analyzing the numerous deformation parameters presented in the literature for the deformation of tetrahedra. We noticed that they can be reduced to a single parameter — the angle of twist, which has not been previously considered as an order parameter at high pressures. We determine the angle of twist as the deviation from the 90-degree angle between two opposite symmetric edges of tetrahedra in  $\alpha$ -quartz. As a result, we were able to find the characteristic features that remained unnoticed in the numerical calculations, specifically, that the rotation angle at high pressures approaches saturation and that the angle of twist, conversely, starts to vary nonlinearly and is therefore the parameter that is mainly responsible for structural instability. This information is important, since despite a number of experimental and theoretical investigations of the amorphization of quartz under pressure,<sup>1–9</sup> there is still no detailed description of such a transition.

The models developed previously for explaining high-temperature anomalies cannot be used to describe the process of amorphization of  $\alpha$ -quartz,<sup>10–13</sup> since they neglect the large distortions of the tetrahedra. In our valence-force model of the deformation of  $\alpha$ -quartz, which takes account of the distortion of the tetrahedra, the parameters related

with the smallest force constants and therefore vary most strongly with pressure play the main role. For example, if the main force constants are considered, then the constant of the Si–O bonds is much larger than the force constant of the O–Si–O angles, and the latter constant is much greater than the force constant of the Si–O–Si angles. For this reason, for our model we employ as the key parameters the rotation angle, which is related with the force constant of the Si–O–Si angle, and the angle of twist, which is responsible for deformation inside tetrahedra and is related with the force constant of the O–Si–O angles. To give a complete description of the structure of quartz it is necessary to introduce four additional parameters — two symmetric O–Si–O angles and two Si–O bond lengths. According to the experimental data, these four parameters are virtually pressure-independent at high pressures,<sup>14</sup> and for this reason we shall assume them to be constant. All parameters are relative and are measured from the parameters of ideal  $\beta$ -quartz with the Si–O distance equal to 1.5993 Å. A calculation using existing experimental structural data<sup>14</sup> shows that even at pressures above 3 GPa the rotation angle  $\varphi$  is approximately 100 times greater than the four parameters mentioned above, and the angle of twist  $\tau$ , describing the distortion of the tetrahedra, is approximately 10 times greater than these small parameters. Therefore, in what follows we shall use only the angle of twist to describe the distortion of tetrahedra.

Ordinarily, only the rotation angle is used to construct an analytical model of the deformation of the structure of quartz.<sup>5,10</sup> We shall examine the Gibbs potential, which, besides the rotation angle, also takes account of the angle of twist:

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

where  $v = (V - V_0)/V_0$  is the relative change in the unit-cell volume,  $\theta$  is the Si–O–Si angle, and  $K_{\theta}$  and  $K_s$  are the force constants (in GPa) of the Si–O–Si and O–Si–O angles, respectively. Here we neglect the small off-diagonal force constants. The quantity  $P_{\alpha}$  is the internal pressure that converts the  $\beta$ -quartz structure isothermally into the  $\alpha$ -quartz structure.<sup>15</sup> This potential takes into account the strain arising in the  $\alpha$ -quartz structure as a result of the fact that the Si–O–Si angle at which there is no deformation is  $\theta_m = 147^\circ$  while the corresponding angle in ideal  $\beta$ -quartz is  $\theta_0 = 155^\circ$ . Using the expansion of  $V$  and  $\theta$  in terms of the parameters  $\varphi$  and  $\tau$ , we obtain the Gibbs potential whose variable part has the form

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

where all coefficients are linear functions of pressure. The equilibrium values of  $\varphi$  and  $\tau$  for the minimum of this potential are

$$\varphi = [(-K_{\varphi} - 2g_1g_2/K_{\tau})/(4g_4 - 2g_2^2/K_{\tau})]^{1/2}, \quad (3)$$

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

Using these equations, we shall construct the functions  $\varphi(P)$  and  $\tau(P)$  displayed in Figs. 1 and 2. Analyzing the function  $\varphi(P)$  at high pressures, we find that it approaches saturation as a result of the contribution of the coefficient  $g_4$ , which increases linearly with pressure. Previously, this saturation was presumed on the basis of experimental data,<sup>14</sup> but it was never substantiated. It should be noted that the saturation of the rotation angle with increasing pressure is due to an increase of its effective stiffness  $K_{\varphi\varphi}^* = \partial^2\Delta G/\partial\varphi^2$ , which attests to an increase in the stability of the structure and cannot be

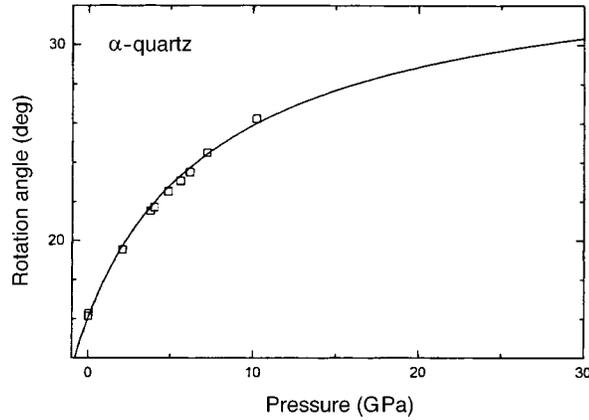


FIG. 1. Rotation angle  $\varphi$  of SiO<sub>4</sub> tetrahedra in  $\alpha$ -quartz versus pressure, calculated using Eq. (3). The squares show the experimental data of Ref. 14; at higher pressures, for trigonal quartz the silicon and oxygen coordinates have not yet been determined.<sup>16</sup>

attributed to the onset of instability. It is evident from the pressure dependence  $\tau(P)$  that at high pressures the angle of twist of tetrahedra starts to grow nonlinearly, and therefore the effective stiffness of the angle of twist  $K_{\varphi\varphi}^* = \partial^2 \Delta G / \partial \tau^2 = K_\tau$  and, with it, certain other elastic moduli decrease, and an instability giving rise to a disordered structure can arise. To check this hypothesis we performed calculations of the lattice dynamics. These calculations were performed not with the interatomic potentials, as is ordinarily done, but rather using the valence-force field. This approach makes it possible to obtain the pressure dependence of the force constants in an explicit form. The force field of an  $\alpha$ -quartz crystal is described in Ref. 17 using the scaled force constants  $K_{q_i, q_j}^0$  of molecular silicate clusters calculated by quantum-chemical methods.

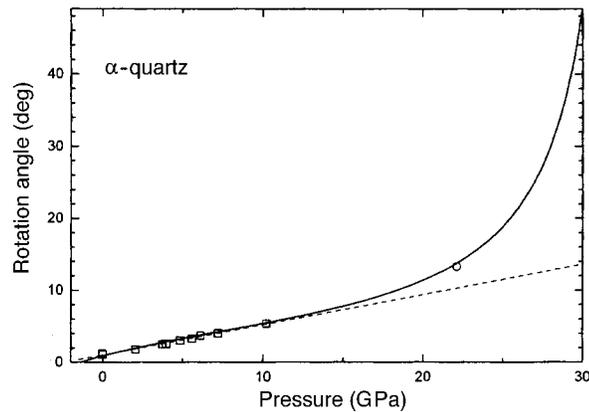


FIG. 2. Angle of twist  $\tau$  of SiO<sub>4</sub> tetrahedra in  $\alpha$ -quartz versus pressure, calculated using Eq. (4). The squares show the experimental data of Ref. 14. The circle at 22 GPa shows the average angle of twist  $\tau_{A_1}$  for the triclinic phase, calculated using the structural data of Ref. 19. For clarity, the dashed curve shows the linear dependence.

In our calculations we employed the indicated force constants, to which, in order to take the pressure into account, we added the second derivatives of the term  $PV$  in the Gibbs potential with respect to the normal coordinate  $q_i$  about the equilibrium positions of the atoms, determined by the parameters  $\varphi(P)$  and  $\tau(P)$  from Eqs. (3) and (4). A similar procedure was performed in Ref. 18. As a result we obtained the pressure-dependent effective stiffnesses of the normal coordinates

$$K_{q_i, q_j}^* = K_{q_i, q_j}^0 - P(\partial^2 V / \partial q_i \partial q_j).$$

The low-frequency transverse acoustic mode in the direction  $[\xi, \xi, 0]$  in the Brillouin zone was calculated using these effective stiffnesses and the matrix of the kinematic coefficients, which are pressure-dependent. It was found that the velocity of an acoustic wave near the point  $\Gamma$  is determined by the torsional stiffness  $\nu \sim (K_{\tau E_1, \tau E_1}^*)^{1/2}$  (where the parameter  $\tau_{E_1}$  is discussed below) and approaches zero with increasing pressure. The form of these soft acoustic oscillations is a sum of the amplitudes of the torsional transverse wave, which mainly entails displacements of the oxygen atoms, and an acoustic transverse wave, in which it is primarily the Si atoms that are displaced. This softening can give rise to the appearance of imaginary frequencies of the torsional modes and therefore instability of the tetrahedra with respect to twisting and then to amorphization.

It was recently ascertained that, according to experimental<sup>16</sup> and theoretical<sup>19</sup> investigations, a triclinic phase forms at 21 GPa prior to amorphization. Calculation of the coordination of the atoms in this phase showed that one of the three Si atoms in a cell is in fivefold coordination, very close to that described in Ref. 20. Thus at a triclinic transition some Si atoms are transferred into a fivefold coordination. The torsional oscillations in the soft modes described above can lead to such a transition. We shall determine the particular parameters that are responsible for the transition to the triclinic phase.

Each of the three tetrahedra of a cell in  $\alpha$ -quartz has one degree of freedom associated with twisting. Three degrees of freedom give rise to different twisting  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  of the three tetrahedra in a cell in  $\alpha$ -quartz; this gives rise to three torsional parameters  $\tau_{A_1} = (\tau_1 + \tau_2 + \tau_3)/3$ ,  $\tau_{E_1} = (\tau_2 - \tau_1)/2$ , and  $\tau_{E_2} = \tau_3 - \tau_1/2 - \tau_2/2$ , which contain static and dynamic components. The static part determines the equilibrium parameters of the structure, and the dynamic part determines the vibrations about these equilibrium positions, which make a contribution with a definite amplitude to the normal modes of the crystal. The static part of the average angle  $\tau_{A_1}$  was previously defined as the twist. The static parts  $\tau_{E_1}$  and  $\tau_{E_2}$  are zero in  $\alpha$ -quartz and nonzero in the triclinic phase. Our calculations, using structural data for the triclinic phase,<sup>19</sup> showed that the main torsional parameter is  $\tau_{E_1}$ . This parameter leads to the same increase of the angle  $\tau_2$  and decrease of the angle  $\tau_1$ , so that the average angle  $\tau_{A_1}$  continues to fall on the curve in Fig. 2. The soft modes giving rise to a transition to the triclinic phase contain the symmetry-breaking shear modes, which contain a large contribution from the  $E$ -type torsional vibrations as well as from the longitudinal modes, which are responsible for the volume deformation of the cell to which the  $A_1$ -type torsional vibrations contribute. The transition to the triclinic phase strongly intensifies the amorphization process, since because of symmetry breaking the torsional parameter  $\tau_{A_1}$  contributes not only to the bulk modulus but also to the shear modulus, sharply decreasing it. Amorphization of this new triclinic structure occurs with a further increase of the pressure above 21 GPa. In view of the fact that x-ray diffraction

analysis shows nucleation of the amorphous phase even at 15 GPa,<sup>6</sup> the transition to the triclinic structure can be regarded as an intermediate stage of amorphization.<sup>2</sup>

In Refs. 21 and 22 it is assumed that an elastic instability at 25 GPa, at which the frequency of the soft acoustic modes becomes imaginary in the entire Brillouin zone, gives rise to amorphization of the  $\alpha$ -quartz structure. In analyzing the microscopic origin of the softening of the phonon modes, these authors neglect the angle of twist. In our view this model is incomplete, and the authors themselves are of the opinion that it is hypothetical.<sup>3</sup> Other authors<sup>1</sup> assert that amorphization starts at a lower pressure, 21.5 GPa, because of dynamic instability, where the frequency of the soft mode becomes imaginary near the point  $(1/3, 1/3, 0)$  in the Brillouin zone. On this basis we believe that the completely symmetric  $\tau_{A_1}$  and incompletely symmetric  $\tau_{E_1}$  torsional oscillations make the main contribution to the elastic and dynamic instability, irrespective of which one plays the main role in the amorphization process and in the shear instability, which gives rise to the transition to the triclinic phase.

In conclusion, we have proposed a new valence-force model of the deformation of  $\alpha$ -quartz, taking account of the distortions of the tetrahedra. According to this model the rotation angle of the tetrahedra at high pressures tends to saturation and therefore the effective stiffness of the structure with respect to this angle increases, which attests to an increase in the stability of the structure and cannot lead to instability. At the same time the smaller parameter — the angle of twist — starts to increase nonlinearly with pressure, and this results in softening of the low-frequency acoustic branch and leads to instability of the tetrahedra with respect to twisting, which gives rise to a transition to the triclinic phase and then to amorphization of the structure.

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