Molecular and lattice dynamical study on modulated structures in quartz

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It is shown that atomistic simulations using the Tsuneyuki potential for silica (SiO_2) correctly reproduce the major experimentally observed properties of the incommensurate (INC) phases in quartz, such as the phase sequence, the direction of the modulation, the coupling of the soft optic with the TA modes, the dispersion surface anisotropy, the stress dependence of the transition temperature, etc. The obtained phase diagram is topologically equivalent to those predicted from general INC phase theories. At high temperature, our results give a short period modulation with $k \approx b/3$ as predicted by the new model for the origin of INC phase in quartz [Aslanyan *et al.*, J. Phys.; Condens. Matter **10**, 4565 (1998); **10**, 4577 (1998)].

Introduction. Silica (SiO_2) is an important material in many application fields and the crystal form of SiO_2, quartz, has been widely used as an insulating material as well as in piezoelectric and optical devices. The $\alpha - \beta$ phase transition from a trigonal D_3 to a hexagonal D_6 structure at $T_c = 846$ K has been studied for more than a century. Therefore the discovery of the incommensurate phase (INC phase) in the late 1970's was a surprise, and has awakened fresh interest in the investigation on quartz (see Refs. 1 and 2). Compared to other crystals, the INC phase in quartz has the following peculiarities: (i) The INC modulation wavelength is very long (more than 30 times the unit cell length) and is the longest one among tens of the crystals which are known to have INC phase.[1] (ii) It appears at high temperature between β and α phases and only in a very narrow temperature interval, $T_c = 846$ K $< T < T_i = 847.4$ K on cooling (and narrower on heating).

From the phenomenological theory based on the Landau free energy expansion, Aslanyan and Levanyuk[3] showed that the origin of the INC phase is the linear coupling between the gradient of the order parameter of the $\alpha - \beta$ transition η and the transverse acoustic phonon TA(C_{66}),

$$\frac{\partial \eta}{\partial x}(u_{xx} - u_{yy}) - 2\frac{\partial \eta}{\partial y}u_{xy}, \qquad (1)$$

where η, is the lowest optic phonon which represents the rotation of SiO_4 tetrahedra around the twofold axis in the $x - y$ plane. Because of this coupling, the softening of the optic mode pushes down the TA(C_{66}) phonon branch which freezes at a *certain* point k on Σ line before the optic soft mode freezes at the Γ point. In x-ray and neutron diffraction experiments,[4,5] satellite peaks were observed close to the Γ point on Σ lines at $k \approx b/30$ (**b** is the reciprocal lattice vector) and on cooling their intensity start increasing at about $T_i = 847.4$ K. This interpretation has been widely accepted as the origin of the INC structure in quartz. However, it was pointed out that there exist not a few experimental facts which remain unexplained and also not compatible with the current model.[6−8] One of the crucial disagreements is the existence of the acoustic displacement u_z along the hexago-

nal z direction in the observed modulated structure because it is not expected from Eq. (1).[9] To solve this and other problems, a new model was proposed by Aslanyan *et al.*,[6,7] which claims that the observed satellite at $k \approx b/30$ is not the fundamental modulation but the third harmonics of a much shorter fundamental modulation brought on by the freezing of the lowest TA branch near $k = b/3$.

In this respect, it is important to investigate what kind of modulation is expected in quartz from a microscopic point of view. Fortunately, in the case of silica (SiO_2), an exceptionally reliable interatomic potential has been given by Tsuneyuki *et al.*[10] This potential was obtained from the first-principle calculations for a SiO_4 cluster, and its validity has already been tested in a number of lattice dynamics and molecular dynamics studies.[10−17] It has successfully reproduced homogeneous stable structures of various polymorphs of crystalline silica,[10−12] a negative Poisson ratio,[12−14] an $\alpha - \beta$ transition,[11,14,15] a thermal expansion of quartz,[15,16] and the boson peak of amorphous silica.[17] Recently, we have shown a numerical method convenient for simulation of modulated phases.[18] However, as far as we know, no other numerical studies using realistic potentials have been performed on the possibilities of modulated phases and their physical properties.

Simulation details. In this paper, we perform the lattice, relaxational, and molecular dynamics (LD, RD, and MD) studies. LD gives the vibration modes of an infinite lattice, and enables us to analyze the phonon dispersion relations and eigenvectors, but it does not account for the anharmonicity. MD includes the anharmonicity but it can treat only a very small volume of the crystal. We use the RD method[19] to find the phase diagram at 0 K, and investigate the stability of the found equilibrium phases at finite temperatures by MD. Combination of these three methods enabled us to carry out a comprehensive study.

In RD, we use a computational cell of up to $12 \times 12 \times 1$ unit cells in order to find various modulations with period up to 12 unit cells. One unit cell in the z direction is enough because the INC modulation wave vector of quartz is known to be in the (k_x, k_y) plane.[2] In MD and LD studies we focus on short-periodic modulated structures, so that it is enough to
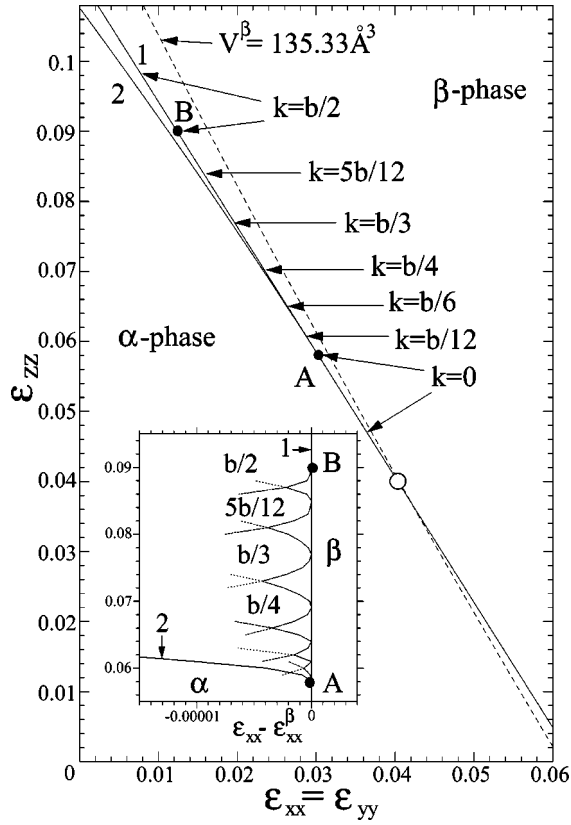
FIG. 1. Phase diagram at 0 K. In the gap between lines 1 and 2, both α and β phases are unstable (LD). The open circle indicates the $\alpha-\beta$ transition under uniform strain.(Ref. 14) Inset: the topology of the modulated/INC phase diagram close to the line 1 (RD).

take $6\times6\times4$ unit cells in MD and up to $3\times3\times1$ unit cells in LD. In all cases the periodic boundary conditions are used. In MD, the Parrinello-Rahman scheme[20] is employed using the external stresses as parameters.

The phase diagram at zero temperature is presented in Fig. 1 in strain space $\varepsilon_{xx}(=\varepsilon_{yy})$ and ε_{zz}. The lattice parameters can be calculated as $a=a_0(1+\varepsilon_{xx})$ and $c=c_0(1+\varepsilon_{zz})$, where $a_0=5.00582$ Å and $c_0=5.53840$ Å are the equilibrium lattice parameters of α-quartz at 0 K used in Ref. 16. The phase diagram obtained in the present study (Fig. 1) was found to be very rich. The authors of Ref. 14 reported that the critical unit cell volume at which a β to α transition takes place as $V^{\beta}=135.33$ Å^3. However, this value was found for uniform strain $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{zz}$ at about 0.04 (open circle in Fig. 1). The dashed line in Fig. 1 is the line of constant volume $V=V^{\beta}$, while the solid lines 1 and 2 were obtained by *independent* variations of ε_{xx} and ε_{zz}.

By RD and LD methods, we found that β quartz is stable in the region to the right of line 1 and α quartz in the region to the left of line 2. Lines 1 and 2 merge together at point A. In the gap between these lines, both α and β phases are unstable.

In the LD simulation, we observed that the frequency of the lowest acoustic branch (TA$_1$) vanishes on approaching lines 1 or 2 from β or α stability regions, respectively (Fig. 2 shows the former case). Vanishing always occurs on the Σ line in agreement with the experimental observations.[4,5] If
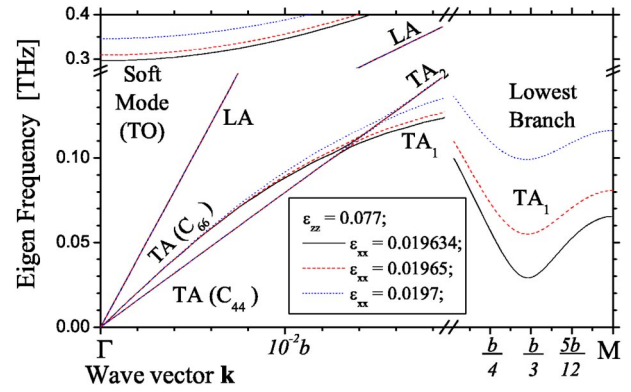

FIG. 2. Dispersion curves close to the transition point from β to the INC phase with $k\approx b/3$ (LD). Near the Γ point, the lowest branch is TA(C$_{44}$), and it anticrosses TA(C$_{66}$) at about $k=1.4\times10^{-2}b$. Due to the interaction of the soft optic mode and the acoustic modes, the lowest branch TA$_1$ freezes at $k\approx b/3$.

line 1 is crossed below point A ($\varepsilon_{zz}<0.058$) then the optic soft mode vanishes at the Γ point and β to α transition takes place. On crossing between points A and B ($0.058<\varepsilon_{zz}<0.090$), the TA$_1$ frequency vanishes at a point on the Σ line between Γ and M points, and modulated phases with $0<k<b/2$ appear. Above point B ($\varepsilon_{zz}>0.090$), the TA$_1$ frequency vanishes at the M point ($k=b/2$). Points of the transition from β to modulated phases with different k are shown in Fig. 1 by arrows.

A RD study shows that crossing line 1 from the right results in a second-order phase transition. The new stable phase has a modulation wave vector equal to the wave vector of the TA$_1$ freezing point found by LD, i.e., the results of RD and LD are in excellent agreement.

The inset in Fig. 1 shows the stability regions of the modulated phases found by RD. Note that all possible phases compatible with the computational cell size $12\times12\times1$ are present. For the abscissa in the inset we use $\varepsilon_{xx}-\varepsilon_{xx}^{\beta}$, where ε_{xx}^{β} is the abscissa of line 1, which is the envelope for the stability regions of various INC phases. A remarkable fact is that the phase diagram of the modulated phases presented in the inset of Fig. 1 is topologically equivalent to the theoretically found phase diagrams of, e.g., the discrete frustrated ϕ^4 (DIFFOUR) model[21] and the elastically hinged molecule (EHM) model.[22] Therefore, general properties of the modulated phases, such as, e.g., "devil's staircase" behavior, etc., can be understood from those theoretical studies. Points A and B are the Lifshitz points. Close to line 1, the boundaries of stability regions of the modulated phases are the square parabolas tangent to line 1 and, in the vicinity of point A, lines 1 and 2 split quadratically. This means that the stability region becomes significantly narrower for smaller k.

Some features of dispersion curves and their dynamics on approaching phase transition are illustrated in Fig. 2, where the results of LD for the strains $\varepsilon_{zz}=0.077$ and $\varepsilon_{xx}=0.019634$ (solid line), $\varepsilon_{xx}=0.01965$ (dashed), and $\varepsilon_{xx}=0.0197$ (dotted) are shown. These points are inside the stability region of β phase, close to line 1 (see Fig. 1), and the lowest branch is about to freeze at the point of Σ line with $k\approx b/3$. This branch is very low along the whole Σ line
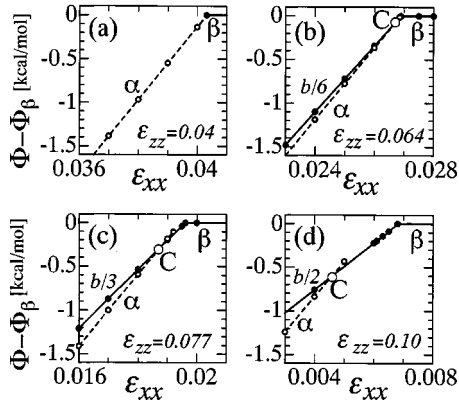
FIG. 3. Comparison of energies of stable phases Φ with energy of the β phase Φ_β for different ε_{zz} (RD).

(below 0.15 THz), and is highly anisotropic within the Brillouin zone. The left part of Fig. 2 shows the dispersion of the low frequency branches near the Γ point. Note that the lowest TA branch is TA(C_{44}), whose eigenvector is primarily the acoustic displacement u_z. This agrees with a number of elastic stiffness measurements[23] which show that the lowest branch near the Γ point is not TA(C_{66}) but TA(C_{44}) for temperatures above ~ 770 K.

As one can see in Fig. 2, on approaching the stability limit of the β phase, the optic soft mode frequency decreases and, due to the interaction given in Eq. (1), the TA(C_{66}) branch bends downward and as a result it anticrosses the TA(C_{44}) branch at about $k = 0.014b$. Although, just after the crossing, the acoustic eigenvector of TA$_1$ is almost equal to that of TA(C_{66}) (i.e., only in the $x-y$ plane), for larger k, LD showed that the center of gravity of a unit cell gradually acquires the z displacement as $|u_z|^2 \sim k^2$. Just after the transition into the three-periodic modulated phase [at, e.g., $(\varepsilon_{xx}, \varepsilon_{zz}) = (0.0196, 0.077)$, very close to line 1 in Fig. 1], RD gives a static modulation pattern with the acoustic nature of $(|u_x|^2, |u_y|^2, |u_z|^2) = (0.24, 0.74, 0.02) |\vec{u}|^2$, that resembles the profile of the acoustic eigenvector of TA$_1$ branch in the β phase at $k \approx b/3$. The z component of the pattern increases rapidly after the transition: on going deeper inside the modulated phase area the components in the above relation become of the same order of magnitude. The existence of u_z component agrees with the observed satellite pattern.[5] If the interaction given by Eq. (1) is the sole origin of INC structure, the freezing of the branch TA(C_{66}) would not give the acoustic displacement u_z.

The energies of different phases are compared in Figs. 3(a)–3(d) as functions of ε_{xx} for $\varepsilon_{zz} = 0.04$, 0.064, 0.077, and 0.1, respectively. The energy difference $\Phi - \Phi_\beta$, where Φ_β is the energy of β phase, is presented. In (a), ε_{zz} is below point A in Fig. 1, and β to α second-order phase transition takes place. In (b)–(d), upon a decrease of ε_{xx}, transitions from β to modulated phases with wave vectors $b/6$, $b/3$, and $b/2$, respectively, take place. The energy lines of the modulated phases and the α phase intersect at point C. The α phase is stable to the left from this point. Note that the region of the stable modulated phase is wider for the larger modulation wave vector.

We found that, with a decrease in ε_{xx} and ε_{zz}, any modulated phase eventually transforms into the α phase (first-order lock-in transition). With an increase of strains, the α phase transforms into a modulated phase if ε_{zz} is above point A (first-order transition) and then into a β phase (second-order transition). The change in strains means a change in the unit cell volume, so that it corresponds to the change in temperature.[14] Thus, the obtained phase transformations reproduce the phase transformations observed experimentally on cooling and heating.[1,2]

A finite temperature MD calculation on the $\alpha - \beta$ transition has been done by Tsuneyuki *et al.*[10] using a constant pressure and a constant temperature method, and they obtained an abrupt change in the expansion coefficient at $T_c = 850–900$ K. In the present study, a constant *anisotropic* stress and a constant energy calculation was used. First, we rebuild the phase diagram shown in Fig. 1 into the diagram in stress space at 0 K and then, by slow heating of α phase for different external stresses $\sigma_{xx} = \sigma_{yy}$ and σ_{zz}, we found that the temperature of transition to β phase is

$$T = 840 - 200\sigma_{xx} - 110\sigma_{zz}, \qquad (2)$$

where stresses are in GPa and temperature is in K. In this paper, applying a positive stress corresponds to volume expansion. The stress dependence agrees reasonably well with the experimentally found relation $\partial T/\partial \sigma_{xx} \approx 2(\partial T/\partial \sigma_{zz}) = -0.14 \pm 0.02$ K/MPa.[5,24]

Discussion. We now discuss the influence of temperature on the stability of various modulated phases. Calculations at $T = 0$ K by Smirnov and co-workers[14,15] show that the β to α transformation in quartz is due to a change in the shape of the effective potential from single well to double well, and the height of the potential barrier between the wells gradually increases on going deeper into the α phase.

Our results suggest qualitatively the same mechanism for the transformation from β to a modulated structure. At a finite temperature, the stable α or modulated phase can appear only when the height of the potential barrier between the wells is greater than thermal energy. The barrier height can be estimated for different modulated phases by the energy $\Phi - \Phi_\beta$ (see Fig. 3) and compared with $k_B T_c$, which is 1.7 kcal/mol for the transition temperature $T_c \approx 850$ K. One can see from Fig. 3 that the energy barrier at point C decreases rapidly with a decrease of the modulation wave vector. For $b/2$, $b/3$, and $b/6$ it comprises 0.65, 0.3, and 0.07 kcal/mol, respectively. For $k = b/12$ (not shown in Fig. 3), the height of the potential barrier is 0.01 kcal/mol, i.e., two orders of magnitude smaller than $k_B T_c$. On increase of temperature, the possible interval of stability of a modulated phase will become narrower or it can disappear completely resulting in the direct transition between β and α phases. Therefore, the smaller is the modulation wavevector k, the lower is the temperature at which this modulation is swept by the thermal fluctuations. In other words, it is highly improbable to observe phases with a small modulation wavevector at high temperatures.

To illustrate this, in Fig. 4 we show the temperature dependence of lattice parameter a obtained by MD simulation
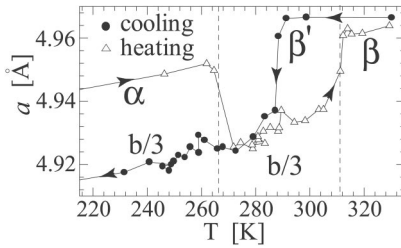
FIG. 4. Temperature dependence of lattice parameter a in the vicinity of the phase transition (MD). Stress is chosen so that the $\alpha - \beta$ transition takes place at about room temperature.

at a given stress $(\sigma_{xx}, \sigma_{zz}) = (-0.9, 6.3)$ GPa. For this stress, from Eq. (2), the $\alpha - \beta$ transition is expected to be at room temperature (much lower than real $T_c \approx 850$ K). and the transition to a stable $3q$-modulated phase with $k = b/3$ is observed both on cooling and heating, with the stability interval about 40 K. However, even at this temperature, and for any other set of $(\sigma_{xx}, \sigma_{zz})$ giving $T_c \approx 300$ K, we could not find stable modulated phases with a modulation wave vector smaller than $k = b/3$.

As mentioned above, another important result of the present study is the existence of the acoustic displacement u_z in the modulated phase with $k \approx b/3$. In the new model,[6] the appearance of u_z is attributed to the higher order interactions between η and the TA(C_{44}) branch such as

$$\eta \left[\left(\frac{\partial \eta}{\partial x} \right)^2 - \left(\frac{\partial \eta}{\partial y} \right)^2 \right] u_{yz} + 2 \eta \frac{\partial \eta}{\partial x} \frac{\partial \eta}{\partial y} u_{xz} .$$

Since this term is proportional to $k^2 \eta^3$, its influence becomes more significant for larger k, and it will give rise to the third harmonics when the order parameter η gets larger. Therefore, for the fundamental modulation at $k = b/3 + \kappa$ ($\kappa \ll b$ is a small misfit vector), its third harmonics with $k = 3(b/3 + \kappa) = 3\kappa \ll b$ will be observed as a long period modulation.

In conclusion, we correctly reproduced many experimentally observed properties of INC phases: phase sequence, modulation direction, dispersion anisotropy, coupling of the soft optic with the TA modes, stress dependence of the transition temperature, etc. The obtained phase diagram is topologically equivalent to the theoretically predicted ones.[21,22] At high temperature, our results have shown that the wave vector of the stable modulation would be $k \approx b/3$, and that a long period such as $k \approx b/30$ is highly improbable for the fundamental modulation in quartz since the transition temperature is too high to make a long period modulation stable. The observed satellites at $k \approx b/30$ would be the third harmonics of the fundamental modulation, as suggested by the new model for the origin of the INC phase.[6,7,25]

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