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Lattice dynamics and thermal expansion of quartz

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The mechanism of the thermal expansion and the α-β phase transition of quartz are jointly studied within the framework of a lattice-dynamical treatment using the pair-wise potential by Tsuneyuki *et al.* [Phys. Rev. Lett. **61**, 869 (1988)]. This shows that the essentially anomalous thermal expansion of quartz originates from the low-frequency phonon modes most of which have negative Grüeneisen coefficients. The main factor driving the α-phase structure variation at heating is the rotation of the SiO_4 tetrahedra towards their β-phase positions. The volume variation follows this process thus keeping the static pressure small. The model reveals that at $T>430$ K a number of the phonons have imaginary quasiharmonic frequencies being governed by a double-well potential. This result does not suggest any large-scale lattice instability, and just indicates that the relevant vibrations are essentially anharmonic and that the actual crystal structure is of a dynamically averaged character. The contribution of such modes to the free energy has been included by the extension of the quasiharmonic theory proposed by Boyer and Hardy [Phys. Rev. B **24**, 2577 (1981)]. Then the accurate free-energy optimization with respect to all the structural parameters provides the α-quartz structure at $T<T_c$. We reveal that there is no free-energy minimum in the α structure at $T>T_c\approx 850$ K, but it exists in the β phase at $850\ \mathrm{K}<T<1100$ K. Taking into account the discovered negative Grüeneisen constants our approach provides a natural explanation for the negative thermal expansion of the β quartz. [S0163-1829(99)02505-9]

I. INTRODUCTION

Despite the number of experimental and theoretical studies of the α-β structural phase transition (SPT) in quartz, its microscopic nature is not yet completely clarified. Moreover, the true nature of the high-temperature β phase remains an unanswered and existing problem.

Recently a model for simulation of the structural and dynamical properties of silica was proposed by Tsuneyuki *et al.*[1] This model represents the potential function of the condensed silica as a sum of pair-wise interactions described by simple analytic expressions with the parameters determined from the *ab initio* molecular cluster study. Below we shall refer to this model as the Tsuneyuki potential model (TPM). Molecular dynamics (MD) simulations[2] using TPM beautifully agree with the observed properties of the α-β SPT: both the critical temperature and the volume increase were well reproduced.

However, the MD method is not quite suitable if one tries to reveal the microscopic nature of the phenomena. MD results are of statistically average character and depend essentially on the number of particles taken into consideration. Thus, it is not easy to conclude from these results the microscopic pattern of the phenomena under study.

The lattice dynamics (LD) modeling dealing with the infinite regular crystal lattice is free of these shortcomings inherent to the MD method. The central objects of the LD theory are phonon modes which are both experimentally observable and microscopically obvious. The LD approach becomes a very powerful method if one can extend it by a proper consideration of the anharmonicity. In this paper, the results of the LD treatment (using TPM) of the thermal expansion and α-β SPT in quartz are presented.

II. STATIC ENERGY CONSIDERATION

The crystal structure of α quartz (space group $P3_22$) is specified by the unit cell dimensions *a,c* and the atomic positions Si (u,0,0) and O (x,y,z). Thus, the static potential energy (PE) of the lattice U is a function of six independent structural coordinates. It was revealed that only two of the structural coordinates vary significantly in course of the thermal expansion and at α-β phase transition. Those are the volume and the SiO_4-tetrahedra rotation. The latter is closely related to the soft-mode eigenvector and in the vicinity of the phase transition it is near-parallel to the vector of the α_1-β-α_2 atomic displacements.[3] All the other structural degrees of freedom involve considerable amount of the SiO_4-tetrahedra distortions and vary insignificantly because those tetrahedra are rather stiff. Thus, in our study we shall focus our attention on two structural coordinates: the unit cell volume V, and the SiO_4-tetrahedra tilt angle η, defined through the parameters *u,x,y,z* by the expression from Ref. 3.

The dependence of U from V and η was studied by *ab initio* methods in Refs. 4, 5, and by TPM in Ref. 6. It was shown that the thermally and pressure-induced crystal structure evolution necessarily involves a strong coupling between these coordinates. It is rather instructive to regard the $U(V,\eta)$ function to be defined by minimization with respect of all other coordinates. This function is plotted in Fig. 1.

The two deep valleys on the $U(V,\eta)$ surface relate to the Dauphine twins. Their minima correspond to the α_1 and α_2 static equilibrium configurations of quartz. The cross section with $\eta=0$ provides $U(V)$ curve for the β-phase configuration. It is worth noting that there is no surface minimum along this curve, its lowest energy point S is a saddle point unstable in the η direction. The dotted line in Fig. 1(b) is the set of minima with respect to η at $V=$const. This line represents the structure evolution at the static negative pressure regime which involves the PE minimization with respect to all the structural parameters at $V=$const. One can see that along this line α configuration transforms into β configuration at point P. This corresponds to the volume value V

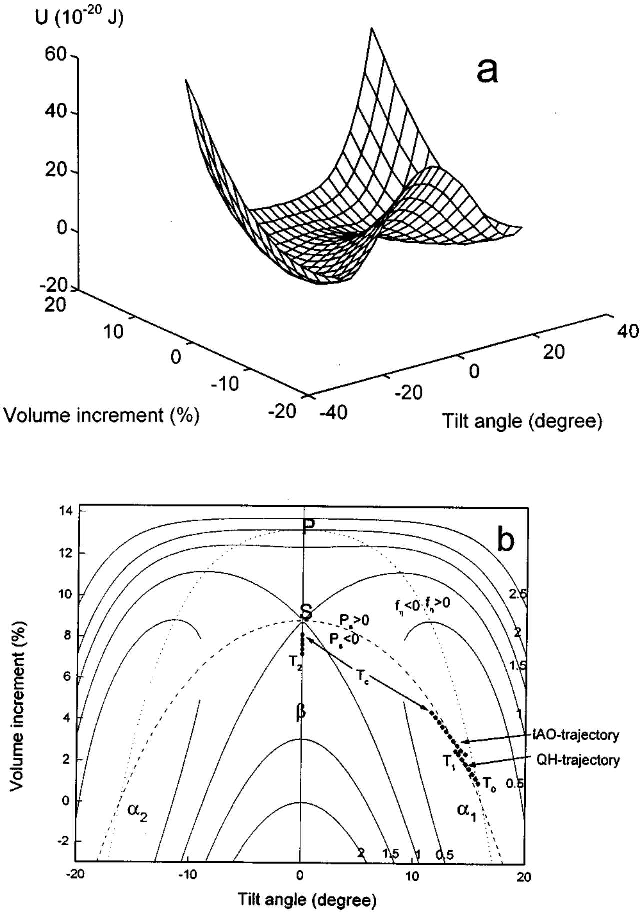

FIG. 1. Potential energy of quartz as a function of volume and tilt angle. (a) The $U(V,\eta)$ surface. (b) Izoenergy contour lines on the V-η plane; the dashed line corresponds to $P_S=0$, the dotted line corresponds to $f_\eta=0$, α_1 and α_2 points are the α-phase static equilibrium configurations, the S-point is the energy minimum β-phase configuration, the P point corresponds to the volume value when the double-minima $V(\eta)$ function transforms into a one-minimum one. The bold dotted lines display the calculated thermal expansion geometry evolution. The critical temperature values are $T_0=0$, $T_1=430\,\mathrm{K}$, $T_c=850\,\mathrm{K}$, $T_2=1100\,\mathrm{K}$. The arrow (denoted by T_c) shows the "geometry jump" at the α-β SPT.

$=V_c$ at which the double-well $U(\eta)$ curve transforms into a one-minimum one.

It was shown[6] that the LD description of the α-β transformation based on the static negative pressure regime enables us to accurately reproduce the variation of all structural and dynamical properties of quartz including such intriguing one as the negative Poisson ratios. At the same time this approach essentially overestimates the β-phase volume V_c: it predicts $(V_c-V_0)/V_0$ of 13% whereas the observed value[7,8] is about 6% (V_0 is the unit cell volume at $T=0$). Evidently, the main failure of the static approach is the neglect of the atomic thermal vibrations which are anharmonic and play an important role in the mechanism of the α-β SPT. Consequently, this approach is incapable of describing the thermal expansion. The present lattice-dynamical study is aimed to overcome the shortcomings inherent to the static consideration and to clarify the role of thermal vibrations in this SPT.

III. THERMODYNAMIC EQUILIBRIUM ANALYSIS

At finite temperature the equilibrium structure is determined by the minimization of the free energy $F=U-TS$ (unlike the only U in the static energy approach). Here and below we use in all the formulae the temperature T in an energy scale omitting the Boltzman constant. Within the quasiharmonic (QH) approximation, which is the most widely used in the theory of the thermal expansion, the entropy contribution is defined by the ω_n phonon frequencies:

$$F=U-T\sum_n \ln[2\sinh(h\omega_n/2T)]. \tag{1}$$

Since the phenomena under consideration take place at high temperature, one can neglect the quantum effects and use the classic expression

$$F=U-T\ln\left[\int\!\!\int\!\!\int_{p,q}\exp\left(-\frac{\Delta U(q)+K(p)}{T}\right)\prod_n\frac{dp_n dq_n}{2\pi h}\right], \tag{2}$$

where q_n and p_n are vibrational coordinates and impulses, $K(p)$ is the kinetic energy, and $\Delta U=U(q)-U(0)$. Within the framework of the QH approximation, after integration over impulses, Eq. (2) assumes the form

$$F=U-T\sum_n \ln(T/h\omega_n). \tag{3}$$

This expression enables us to reveal the main forces driving the thermal expansion. Usually, in "normal" crystals, the ω_n phonon frequencies drop at volume expansion. Thus, the second term in Eq. (3) drives the crystal to extend, whereas the first one keeps the lattice stable (up to the melting limit). The thermodynamic equilibrium condition is written as

$$\frac{\partial F}{\partial V}=\frac{\partial U}{\partial V}-T\frac{\partial S}{\partial V}=P_S-T\gamma_\nu=0, \tag{4}$$

where P_S is the static internal pressure and γ_ν is the volume-dependent Grüeneisen constant defined as

$$\gamma_\nu=-\sum_n\frac{1}{\omega_n}\frac{\partial\omega_n}{\partial V}.$$

In a normal crystal, the positive value of γ_ν is related to the anharmonicity of the interatomic forces: the curvature of the interatomic potentials diminishes at increasing interatomic separation.

It is worth emphasizing that γ_ν may be very small and even negative in the so-called framework crystal structures, which are built up as a frame of stiff corner-connected polyhedra. In some cases such crystals do manifest the negative thermal expansion.[9] Such an "unusual" situation is related to the so-called rigid unit modes (RUM's), which exist in the phonon spectra of the framework crystals and which involve the rotations or translations of the rigid polyhedra. These modes are of low frequency. Thus, they give large contributions to the γ_ν value. As a rule, RUM's have positive derivatives $\partial\omega/\partial V$. It was first noted in Ref. 9. This inherent property of RUM's can be explained by the intrapolyhedron tension contribution.[6]

The high-frequency modes in a framework crystal have the negative (normal) value of $\partial\omega/\partial V$. Thus, the total magnitude of γ_ν is determined as a subtle balance between the negative RUM's contributions and the positive ones from the high-frequency normal modes. The result depends on how many RUM's are there in the phonon spectrum of the crystal.

The detailed analysis[10] shows that almost all the acoustic branches and the considerable part of the low-frequency optic branches in β quartz consist of RUM's. In α quartz many of them transform into quasi-RUM (QRUM). The latter resemble RUM's but they involve a small amount of polyhedra deformations. They also have $\partial\omega/\partial V>0$.

The negative γ_ν value should induce negative thermal expansion, e.g., volume contraction at heating. It would be inevitably so, if there were no V-η coupling. In general, the thermally induced crystal structure evolution involves not only the volume variation but also the microscopic relaxation—the shifts of the mean atomic positions. This relaxation should be taken into account by the minimization of the free energy with respect to internal structural parameters. Let us recall that in the case of quartz only the η variation is of primary importance. Thus, in addition to condition (4), one should consider the condition

$$\frac{\partial F}{\partial \eta}=\frac{\partial U}{\partial \eta}-T\frac{\partial S}{\partial \eta}=f_\eta-T\gamma_\eta=0, \tag{5}$$

where f_η is the force conjugated to η and γ_η is the corresponding Grüeneisen parameter

$$\gamma_\eta=-\sum_n \frac{1}{\omega_n}\frac{\partial \omega_n}{\partial \eta}.$$

As it was noticed above, the dependence $U(\eta)$ has a double-well form at $V<V_c$. There are two minima at $\eta=\pm\eta_0$ corresponding to the two Dauphine twins. For definiteness, let us consider the α-phase corresponding to $\eta_0>0$. It should be noted that the vibration along the η coordinate is a typical QRUM (this is the soft mode driving the SPT) and its frequency would drop when the structure varies from $\eta=\eta_0$ to $\eta=0$. One can expect that all other QRUM's should have the similar behavior. Hence, the corresponding contributions of these modes in γ_η value would be negative. So it can be concluded that the entropy contribution to the free energy [second term in Eq. (1)] causes the thermally average $\overline{\eta}$ to decrease at increasing temperature.

Taking into account the strong coupling between V and η variation one has to consider the conditions (4) and (5) jointly. It can be seen from Fig. 1 that the decrease of η causes the decrease of P_S thus provoking an additional volume expansion (or damping the negative thermal expansion). The total effect results from the competition between these two factors. A quantitative study of the situation must involve an accurate six-dimension free-energy function optimization. Owing to its conceptual simplicity, the adopted TPM enables us to solve this problem without any additional approximations.

We have done an accurate free-energy minimization with respect to all the six independent structural parameters of the quartz lattice. The phonon contribution was calculated by summation over the $7\times7\times7$ grid in the Brillouin zone (BZ). (Further augmentation of the number of points shifts the free energy scale and only slightly changes its relative values.) For the optimization we have used a gradient method evaluating the derivatives $\partial\omega/\partial V$ and $\partial\omega/\partial q$ by the explicit analytic differentiation of the dynamical matrix.

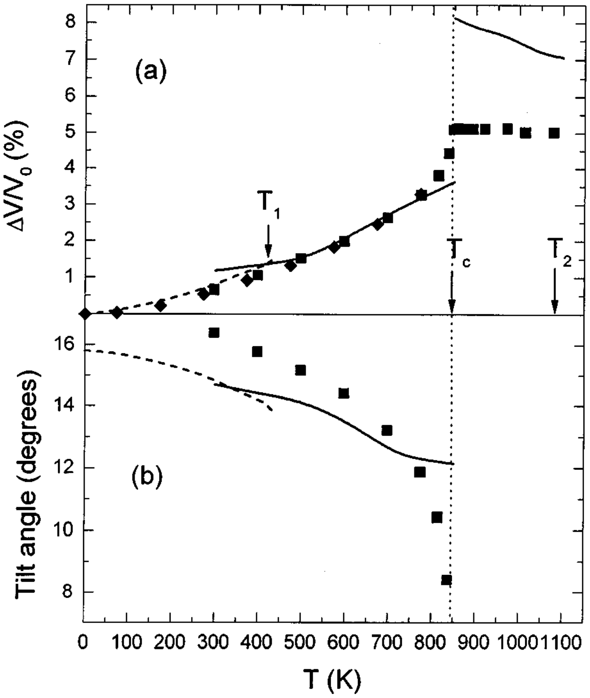

FIG. 2. Volume thermal expansion (a) and tilt angle versus temperature variation (b) in quartz. The theoretical results are shown by dashed lines (QH approximation) and by solid lines (IAO approximation). The scattered experimental data are from Ref. 7 (diamond marks) and from Ref. 8 (bold squares).

A. Quasiharmonic approximation

First we have studied the thermal expansion of α quartz starting from zero temperature by using the quasiharmonic definition of the free energy [Eq. (1)]. We have found the zero-temperature thermodynamic equilibrium configuration ($V=120.60\,\text{Å}^3$) not far from the static equilibrium one ($V=119.38\,\text{Å}^3$). The zero-temperature free-energy minimum corresponds to static pressure of $P_S=9.1\,\text{kbar}$. The calculated $V(T)$ and $\eta(T)$ dependencies are shown in Fig. 2. The obtained V-η QH trajectory is displayed in Fig. 1(b) by bold dotted lines.

Because α quartz has a rather deep potential energy minimum one could expect that α quartz should behave at thermal expansion as a normal crystal in which the phonon thermal pressure [second term in Eq. (4)] drives the crystal to expand, whereas the static internal pressure P_S is positive. However, this is not the case in α quartz. One can see from Fig. 1(b) that with increasing temperature P_S diminishes and becomes negative at $T>330\,\text{K}$. This originates from the negative value of γ_ν [see Eq. (4)]. To elucidate such an unusual situation, let us consider the $\gamma_\nu(\omega)$ frequency distribution defined as

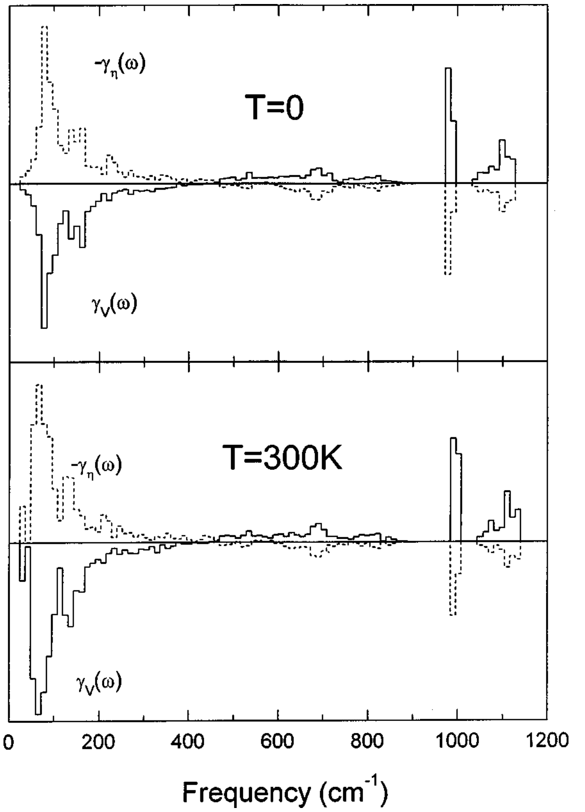

FIG. 3. Calculated Grüeneisen parameters γ_ν and γ_η as a function of phonon frequency at selected temperature in α quartz.

$$\gamma_V(\omega)=-\sum_n \frac{1}{\omega_n}\frac{\partial\omega_n}{\partial V}\delta(\omega_n-\omega). \tag{6}$$

The calculated $\gamma_\nu(\omega)$ functions are shown in Fig. 3. Comparing those calculated at $T=0$ and $T=300\,\mathrm{K}$, one can see that they change very little with the variation of crystal geometry. It is seen that all the modes whose frequencies are lower than 400 cm^{-1} have $\partial\omega/\partial V>0$. The eigenvector analysis shows that all those modes involve a considerable amount of SiO$_4$-tetrahedra rotations. Thus, they are QRUM's (in notation of Ref. 9).

As it was mentioned above, the distinguished feature of the thermal expansion of α quartz is the decrease of the tilt angle with increasing temperature. The calculated η (T) dependence presented in Fig. 2 is in accordance with this. Such a decrease of η is caused by the positive value of $\partial\omega/\partial\eta$. The calculated $\gamma_\eta(\omega)$ distribution [similar to $\gamma_\nu(\omega)$ in Eq. (6)] is also presented in Fig. 3. One can see that the same low-frequency QRUM's cause both γ_ν and γ_η to be negative.

The calculations show that the crystal volume expands despite the negative γ_ν value. It is the decrease of η which causes (due to the strong V-η coupling) the volume expansion of α quartz. Our calculations enable us to estimate the coefficient of such a coupling defined as

$$\frac{\partial\eta}{\partial V}=-\frac{1}{\omega^2}\frac{\partial^2 U}{\partial V\partial\eta}.$$

In α quartz it is equal to about 5°/A^3. Such a rather strong coupling overcomes the tendency to volume contraction coming from the negative γ_ν value.

The high and positive QRUM values of $\partial\omega/\partial\eta$ and the considerable $\eta(T)$ variation lead to the essential softening of the low-frequency QRUM's at heating. The numerical results show that the zone-boundary acoustic modes at the M and A points of BZ are the softest. This peculiarity of the phonon spectra of quartz was early established experimentally[11] and theoretically.[12] In our calculations, this softening leads to the vanishing of $\omega_{TA}(A)$ at $T=T_1=430\,\mathrm{K}$. Beyond this temperature, strictly speaking, the QH approximation ceases to be applicable.

The disappearance of some harmonic phonon frequencies does not mean a destabilization of the lattice and by no means indicates the existence of a phase transition. This only means that those vibrations are essentially anharmonic and are governed by the double-well potential. The phase transition condition still should be tested by the free-energy minimum investigation. The question is how to calculate the free-energy contributions of these anharmonic (with imaginary harmonic frequencies) modes. In the case of quartz we can not neglect these contributions because those harmonically unstable modes spread over a considerable (with a nonzero volume) part of the BZ. When $\omega\rightarrow 0$ such a mode gives an infinite negative contribution to the QH free-energy [see Eq. (3)]. As a result, in the QH approximation the free-energy minimum geometry fall very quickly from α to β configuration. Hence, to treat properly the free energy of quartz at $T>T_1$, one should go beyond the limits of the QH approximation.

B. Independent anharmonic oscillators

The similar situation was found in Ref. 13 for the CaRbF$_3$ lattice. It was proposed there to account the free-energy contributions of the harmonically unstable QRUM's by treating these modes as independent anharmonic oscillators (IAO's). This means that the potential energy is assumed to be a sum of all the phonon mode contributions

$$\Delta U(q)=\sum_n \varphi_n(q_n). \tag{7}$$

For the harmonically stable modes, one can still use the harmonic expression $\varphi(q)=\frac{1}{2}\omega^2 q^2$. For the essentially anharmonic modes (in particular for those with imaginary harmonic frequencies) the high-order terms must be taken into account. We have studied the $\Delta U(q)$ dependence for some unstable modes of quartz at several volume values. All the potentials were found to have a double-well shape which may be described by the expression

$$\varphi(q)=\frac{1}{2}\lambda q^2+\mu q^4. \tag{8}$$

The negative λ values are obtained by the dynamical matrix diagonalization. The anharmonicity parameter μ should be estimated numerically. This value varies from mode to mode. But its variation is not too significant as well as its volume dependence. To simplify the numerical calculations, we assume the μ parameters to be volume independent and

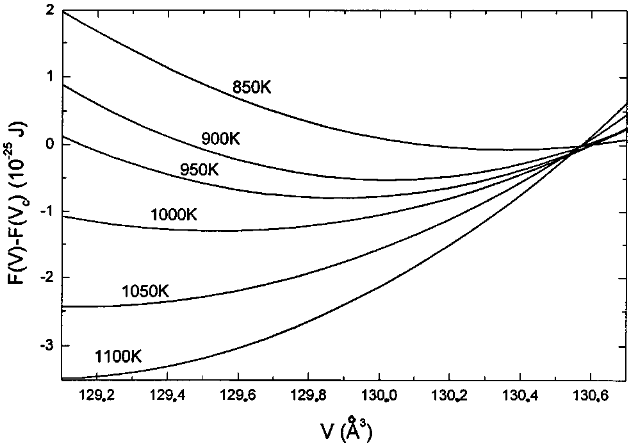

FIG. 4. Free-energy of the α quartz as a function of tilt angle at selected temperatures around the critical point ($T_c = 850$ K).

equal to the average value for all the modes. It is more convenient (see the Appendix) to use instead of μ another parameter $T_\mu = h^{4/3}\mu^{1/3}$. According to our calculations, the mean value of this parameter is $T_\mu = 25$ K in the α phase.

The thermal expansion of α quartz was studied within the IAO approximation by using the optimization of the free energy defined by Eqs. (2), (7), and (8). The details of the calculations are discussed in the Appendix. The $\eta(T)$ and $V(T)$ dependencies thus obtained are presented in Fig. 2. The corresponding V-η IAO trajectory is displayed in Fig. 1(b) by the bold dotted line. One can see that all the main tendencies revealed within the QH approximation are still valid in the IAO approach. But now the crystal is more stable with respect to the α-β transformation. We have found the free energy minimum in the α configuration at increasing temperature up to $T_c = 850$ K. The calculated $V(T)$ and $\eta(T)$ dependencies agree well with the experimental data. At $T \rightarrow T_c$ we have revealed the situation typical for a first-order SPT: the free-energy well becomes more shallow and more flat. At $T > 850$ K there is no minimum at α-configuration. The calculated $F(\eta)$ curves for T around 850 K are presented in Fig. 4.

Thus, at T approaching T_c, the entropy contribution predominates over the potential one, and the lattice configuration falls down into β phase. It is worth emphasizing that we are dealing with the thermally averaged lattice configurations. They by no means correspond to the static equilibrium geometry. The obtained α-β ''geometry jump'' [displayed by the arrow in Fig. 1(b)] takes place at rather high temperature, when many phonon modes are essentially anharmonic.

IV. DISCUSSION

A. Thermal expansion of α quartz

The main factor driving the α-phase structure variation at heating is the rotation of the SiO_4 tetrahedra towards their β-phase positions. The volume change follows this process thus keeping the static pressure small. This also accounts for the relevant Si-O bond shortening. The calculated temperature dependence of Si-O bond lengths and Si-O-Si angle are compared with the experimental data in Fig. 5. One can see that all the main tendencies are well reproduced. The shortening of the Si-O bond length at the α-quartz thermal expansion was often considered as an evidence of existence of some special mechanisms of the Si-O bond stabilization: or by means of the bond-angle interaction[3] either by means of the ionicity augmentation.[14] The model used in this study does not include any special terms. It explains the observed Si-O bond shortening at heating as a purely dynamic effect: the SiO_4-tetrahedra rotation towards their β phase orientation leads to the essential RUM's softening and to the relevant entropy augmentation. Thus, it becomes more and more preferable despite of an inevitable potential energy increase caused by the concomitant bond length shortening. The latter causes the intratetrahedron tension and leads to a volume expansion.

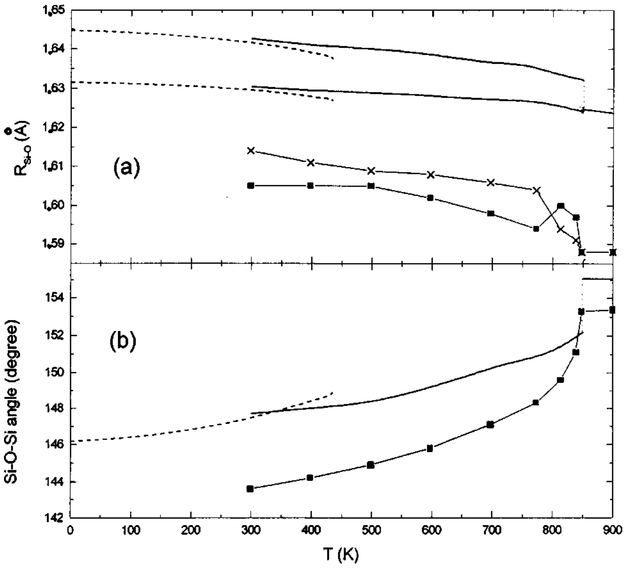

FIG. 5. Temperature dependence of α-quartz Si-O bond lengths (a) and Si-O-Si angle. The theoretical results are shown by dashed lines (QH approximation) and by solid lines (IAO approximation). The scattered experimental data are from Ref. 8.

B. The thermodynamic equilibrium and crystal structure of β phase

The problem of anharmonicity is much more difficult at the search for the free-energy minimum in the β phase, where a considerable part of the phonon modes is harmonically unstable. Now not only the above mentioned zone-boundary modes but whole acoustic branches and zone-center lowest-frequency B_1 (''soft mode'') have imaginary harmonic frequencies. The study of the potential energy variation at large-amplitude atomic displacements has shown that the true potentials of all these unstable modes still have the double-well shape. The potential curves of some such modes are shown in Fig. 6.

The anharmonicity is more pronounced in β phase than in α phase. Numerical evaluations of the anharmonicity coefficient gives for β phase the average value of $T_\mu = 36$ K. We have applied the same IAO model and, by using this value of T_μ have found the free-energy minimum at $T > T_c$. These results are presented in Fig. 7.

There is no V-η coupling in the β phase: the average value of the tilt angle drops to $\eta = 0$ at $T = T_c$. Therefore, in β quartz the negative γ_V value actually drives the negative

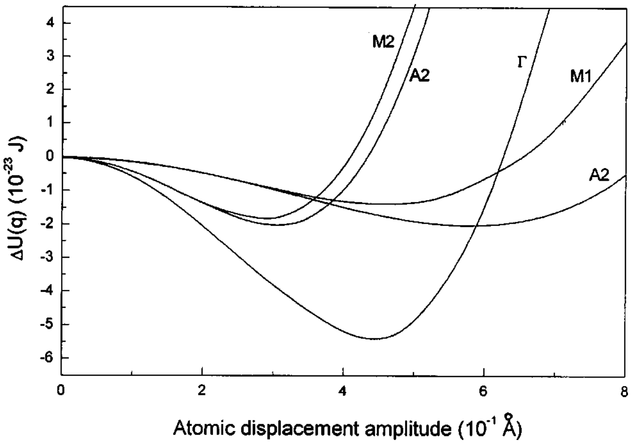

FIG. 6. The potential energy curves for some anharmonic phonon modes in β quartz.

thermal expansion. The calculated $V(T)$ dependence at $T > T_c$ is shown in Fig. 2. Our calculations show (see Fig. 7) that at further heating (at $T > T_2 = 1100\,\mathrm{K}$) there is no free-energy minimum at all. This does not coincide with the experimentally stated melting limit of 1400 K. However, this is a qualitative conclusion only since such a large-scale amplitude atomic motion, as observed in the β phase at high temperature, makes the applicability of the IAO approximation questionable.

The obtained results obviously confirm the opinion that the β phase is a dynamic structure. The atomic vibrations are essentially anharmonic. Many vibrational modes occur into a double-well potential. The theoretical study of such vibrations lies beyond the QH approximation. In particular, it seems ambiguous to treat the INC phase generation in the framework of a quasiharmonic theory when the thermal atomic vibrations are essentially anharmonic near the α-β phase transition in quartz.

C. Role of the intrapolyhedron tension in the dynamics of the framework structures

According to the above results the following properties could be considered as inherent for the framework structures built up from the corner-shared rigid polyhedra: (a) there are a number of RUM's and QRUM's in the phonon spectra, (b) the structure could undergo a thermally induced SPT, so that the rigid polyhedra are tilted in the low-temperature phase, the tilt angle coordinate η is, as a rule, the order parameter (we imply $\eta = 0$ in the high-symmetry phase), (c) there exists a considerable coupling between the V and η variations $\partial^2 U/\partial V \partial \eta > 0$, (d) the derivatives $\partial\omega/\partial V$ and $\partial\omega/\partial\eta$ are positive for all the RUM's and QRUM's.

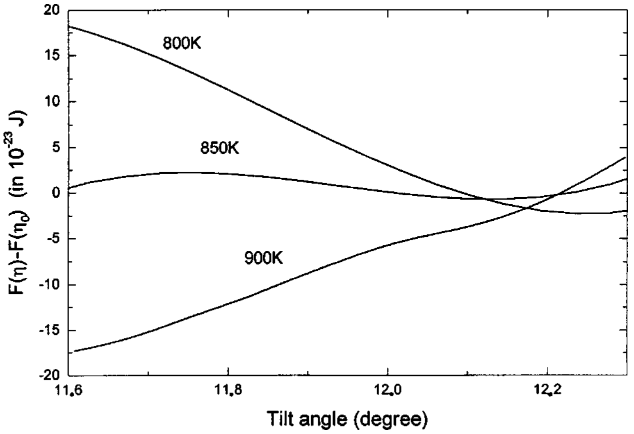

FIG. 7. Free-energy of the β quartz as a function of unit cell volume at selected temperatures.

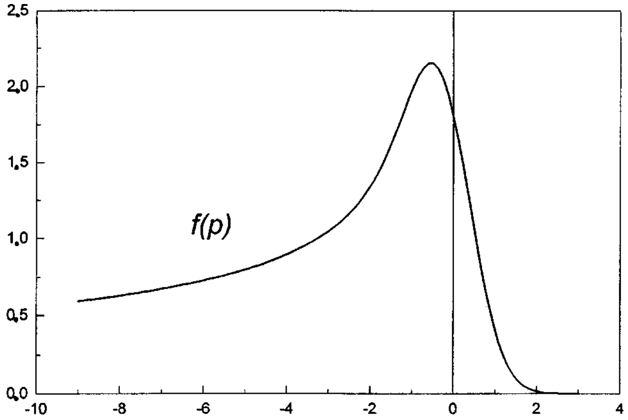

FIG. 8. The calculated values of the integral $f(p)$.

The true temperature-induced crystal structure evolution would result from the minimal free energy condition as a balance between the potential energy and entropy contributions. The latter [second term in Eq. (3)] decreases, when the mean phonon frequency decreases, and becomes more important with temperature increase. Therefore, point d is rather important. It can lead to the nonmonotone volume versus temperature dependence (and even to the negative thermal expansion), and causes the mean η value to drop quickly at heating. This provides the softening of many RUM's.

A quite general explanation can be given for the point d. Actually, being packed within a framework structure, the rigid polyhedra are essentially compressed relatively their free state geometry. For example, the adopted potential model predicts a free SiO_4 tetrahedron to be in equilibrium at Si-O bond length $R = 1.663\,\text{Å}$. Thus, within the crystal lattice $\partial U/\partial R < 0$. We denote this value as internal tension.

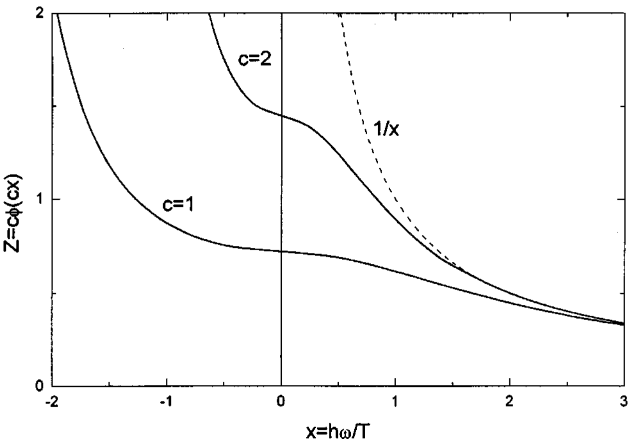

FIG. 9. The free-energy contribution of the anharmonic double-well potential mode, $Z = c\varphi(cx)$, as a function of $x = h\omega/T$ at different c values in comparison with the harmonic dependence $Z = 1/x$.

By definition, RUM does not involve the polyhedron bond length variation. So, if the RUM's amplitude is q, one can conclude that $\partial R/\partial q \approx 0$. At the same time, the second derivative $\partial^2 R/\partial q^2$ is, as a rule, positive and not small. The latter issue follows from a pure geometrical consideration taking into account that the RUM is a rotation of the polyhedra. The contribution of the intra-polyhedron potential to the squared RUM's frequency can be written as

$$\omega^2 \propto \frac{\partial^2 U}{\partial R^2}\left(\frac{\partial R}{\partial q}\right)^2 + \frac{\partial U}{\partial R}\,\frac{\partial^2 R}{\partial q^2}.$$

Since the first term of the above expression vanishes, whereas the second one is negative, the intrapolyhedron interaction destabilises the RUM's. This effect comes from the internal tension and would diminish at R increasing. There are two ways for polyhedra to swell: in the course of a lattice expansion and by means of tilting. That is why the point d is of general validity.

V. CONCLUSIONS

The LD approach based on the TPM enables us to explain all the main peculiarities observed in the thermal expansion and in the α-β SPT in quartz. The following unusual properties related to the thermal expansion of the α phase are revealed: the vibrational pressure tries to compress the lattice whereas the static pressure acts to extend it; at $T > 430\,\mathrm{K}$ some of phonon modes are essentially anharmonic and have imaginary harmonic frequencies. The calculations show that many vibrational modes obey the double-well potential. The IAO approach provides a meaningful estimation of the contributions of such modes to the free-energy.

This theory confirms the existence of the first-order SPT in quartz at T_c near 850 K. The β phase is found to be thermodynamically (but not statically) stable at larger volume and at higher temperature. Thus, the β phase (and even the α phase at $T > 430\,\mathrm{K}$) is an essentially dynamic structure. The theory does predict the negative thermal expansion in the β phase. The above peculiarities are related to the three factors: (i) the phonon spectrum of quartz includes a great part of RUM's and QRUM's providing the dominant contribution to the free energy, (ii) there is a strong coupling between the volume variation and the soft-mode atomic displacements in the α phase, (iii) there are the intratetrahedron tensions which determine the RUM's spectrum versus structure variation dependence.

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APPENDIX: EVALUATION OF THE DOUBLE-WELL POTENTIAL CONTRIBUTION TO THE FREE-ENERGY WITHIN THE IAO-APPROXIMATION

By substituting Eq. (7) into Eq. (2) and after integration over the impulses one obtains

$$F = U - T\sum_n \ln Z_n, \tag{A1}$$

where

$$Z_n = \frac{1}{h}\sqrt{\frac{T}{2\pi}}\int e^{-\phi_n(q)/T}dq. \tag{A2}$$

To calculate this integral with the potential $\varphi(q) = \frac{1}{2}\lambda q^2 + \mu q^4$, let us introduce the following notations:

$$\omega = \mathrm{sgn}(\lambda)\sqrt{|\lambda|},\quad x = \frac{h\omega}{T},\quad c = \left(\frac{T}{T_\mu}\right)^{3/4},$$

$$\text{and}\quad T_\mu = h^{4/3}\mu^{1/3}.$$

Thus defined, ω coincides with the harmonic frequency at $\lambda > 0$, and is negative at negative λ value. Then the Eq. (A2) can be rewritten as follows:

$$Z = c\varphi(cx), \tag{A3}$$

where function φ is defined as

$$\varphi(t) = e^{t^4} f(t^2) \tag{A4}$$

and $f(p)$ is the integral

$$f(p) = \frac{1}{\sqrt{2\pi}}\int e^{-(x^2+p)^2}dx, \tag{A5}$$

which can be easily calculated by means of the Gauss-Christoffel method. The thus obtained function $f(p)$ is shown in Fig. 8. It was used in our numerical calculations.

Let us now consider the dependence of the Z value on the quasiharmonic squared frequency λ and on the anharmonicity coefficient μ. In the Eq. (A3) the multiplier c is the factor of anharmonicity. Thus, $c = \infty$ (e.g. $\mu = 0$) corresponds to the pure harmonic case. At this limit one should obtain the classic expression $Z = 1/x$. The value of Z as a function of x is shown in Fig. 9 for different c values. One can see that for any c value $Z \to 1/x$ if $x \to \infty$. This corresponds to the high-frequency region where $\lambda \gg \mu$, and one can neglect the anharmonicity. At the same time at $c \to \infty$ the curve $Z(x)$ nearly coincides with the $1/x$ curve for all $x > 0$.

The singularity of the harmonic dependence $Z = 1/x$ at x approaching zero restricts the applicability of the QH approximation in the case of a harmonically unstable mode when $x \leqslant 0$. Figure 8 illustrates how the IAO approach provides a smooth extension of the free energy definition into the negative λ region.

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